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Number 22

WATER QUALITY MANAGEMENT IN AQUACULTURE

ISSUED ON THE OCCASION OF THE WORKSHOP ON
WATER QUALITY MANAGEMENT IN AQUACULTURE

ORGANISED BY

CENTRE OF ADVANCED STUDIES IN MARICULTURE
CENTRAL MARINE FISHERIES RESEARCH INSTITUTE
INDIAN COUNCIL OF AGRICULTURAL RESEARCH

HELD AT COCHIN FROM 10 - 13 DECEMBER 1984

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WATER QUALITY MANAGEMENT IN AQUACULTURE

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INTRODUCTION

Water quality includes all physical, chemical and biological factors that influence the beneficial use of water. Where fish culture is concerned, any characteristic of water that affects the survival, reproduction, growth, production, or management of fish in any way is a water quality variable. Obviously, there are many water quality variables in pond fish culture. Fortunately, only a few of these normally play an important role. These are the variables that fish culturist should concentrate on, and attempt to control to some extent by management techniques.

All other things being equal, a pond with 'good' water quality will produce more and healthier fish than a pond with 'poor' water quality. In this manual an attempt is made to define 'good' water quality for fish culture. Information is also presented which will help in determining the potential of a body of water for producing fish, improving water quality, avoiding stress-related fish disease and parasite problems, maintaining fish for research purposes and ultimately producing more fish per unit of surface area. The following discussion of water quality is brief, but an attempt has been made to cover the most important points. Chapter 1 is concerned with general aspects of water quality that influence fish production. The influence of fish feeding on water quality is covered in Chapter 2. Chapter 3 covers pond fertilization and Chapter 4 is concerned with liming. Dissolved oxygen and aeration is treated in Chapter 5. Chapter 6 deals with miscellaneous treatments and procedures for computing doses of chemicals for ponds. Methods of water analysis are presented in Chapter 7.

The information in this manual is essentially a summary of a book on water quality in pond fish culture by Boyd, 'Water Quality Management in Pond Fish Culture'. This book may be consulted for more details and for additional references to the literature on water quality in ponds. Most of the basis for the

book and this manual was research on warm water pond fish culture in the Southern United States. However, all of the principles and methods are general and applicable to fish culture in other regions including culture of fish in brackish water and sea water ponds.

WATER QUALITY AND FISH PRODUCTION

1.1. *Introduction*

The material in this report explains the usual relationships between water quality variables and fish production, setting forth, where possible, ranges of desirable levels of the variables. In addition, the management procedures recommended herein usually will be effective in improving water quality. However, because of unexplained reasons, effects of water quality on fish and the effectiveness of management procedures may be quite different from those reported here. Therefore, fish culturists should not consider the information in this report as the final answer to water quality problems, but merely as suggestions on how to solve these problems. Coldwater fish will not be considered, but coldwater fish generally demand water of much better quality than do warmwater fish.

1.2. *Temperature*

Warmwater fish grow best at temperatures between 25°C and 32°C. Water temperatures are in this range the year around at low altitudes in the tropics, but in temperate regions water temperatures are too low in winter for rapid growth of fish and fish food organisms. For this reason, management procedures such as feeding and fertilizing are halted or reduced in winter. Temperature has a pronounced effect on chemical and biological processes. In general, rates of chemical and biological reactions are doubled for every 10°C increase in temperature. This means that aquatic organisms will use twice as much dissolved oxygen at 30°C as at 20°C and chemical reactions will progress twice as fast at 30°C as at 20°C. Therefore, dissolved oxygen requirements of fish are more critical in warmwater than in cold water. Chemical treatments of ponds also are affected by temperature. In warm water, fertilizers dissolve faster, herbicides act quicker, rotenone degrades faster and the rate of oxygen consumption by decaying manure is greater.

In ponds, heat enters at the surface and so surface waters get heated faster than lower waters. Since the density of water (weight per unit volume) decreases with increasing temperature above 4°C, the surface waters may become so warm and light that they do not mix with the cooler, heavier waters in lower layers. The separation of pond water into distinct warm and cool layers is called thermal stratification. The upper warm layer is called the epilimnion and the lower cooler layer is known as the hypolimnion. The layer of rapidly changing temperature between the epilimnion and the hypolimnion is termed the thermocline. The temperature profile for a thermally stratified pond is shown in Fig. 1.1. In temperate regions large ponds may stratify in the spring and remain stratified until fall. In small, shallow ponds

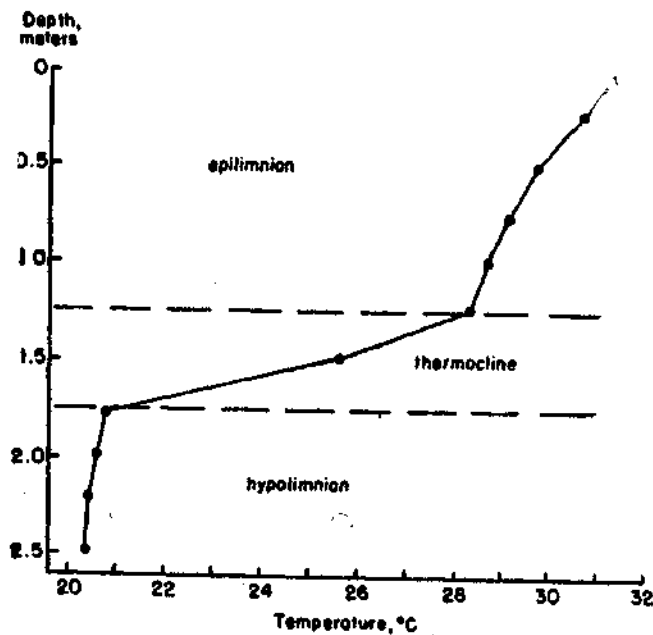


FIG. 1.1. A well developed pattern of thermal stratification in a fish pond. The epilimnion, thermocline and hypolimnion are indicated.

in temperate regions and in tropical ponds, stratification often exhibits a daily pattern. During the day the surface waters warm and form a distinct layer. At night the surface waters cool to

the same temperature as the lower waters and the two layers mix. An extensive discussion on thermal stratification may be found in any standard text on limnology.

In some ponds, the surface waters may reach temperatures of 35°C or more. This is above the optimum temperature for most warmwater fish, but the fish may seek haven from the high temperature in subsurface waters. Fish have poor tolerance to sudden changes in temperature. Therefore, one should not remove fish from water of one temperature and suddenly thrust them into a water of appreciably higher or lower temperature. Often, a sudden change in temperature of as little as 5°C will stress or even kill fish. The effect is usually worse when moving fish from cooler to warmer water. Since temperatures increase with decreasing altitude, one must allow for temperature adjustment when moving fish from high altitude to low altitude waters. Fish readily tolerate gradual changes in temperature. For example, one could raise temperature from 25°C to 32°C over several hours without harming fish, but fish suddenly removed from 25°C water and placed in water of 32°C might die.

1.3. *Salinity*

The term salinity refers to the total concentration of all dissolved ions in a natural water expressed in milligrams per litre. The osmotic pressure of solutions increases with increasing salinity. Fish species differ in their osmotic pressure requirements, so the optimum salinity for fish culture differs to some extent with species. Salinity information on some cultured species of pond fish is presented in Table 1.1.

Fish are highly sensitive to sudden changes in salinity. Fish living in water at one concentration of salinity should not suddenly be placed in water with a much higher or lower salinity. Small fish and fry of most species are more susceptible than adult fish to sudden changes in salinity. Sodium chloride may be used to increase the salinity in fish holding facilities and even in small experimental ponds. Conversely, salinity may be lowered in small scale systems by the addition of water with low salinity. Unfortunately, it is usually not practical to adjust the salinity of

larger fish culture systems, except in brackishwater ponds where seawater may be introduced by gravity flow or tidal movement.

TABLE 1.1. Highest concentrations of salinity which permit normal survival and growth of some cultured food fish

Species	Salinity (mg/litre)
<i>Carla catla</i> (catla)	.. slightly brackishwater
<i>Labeo rohita</i> (roha)	.. slightly brackishwater
<i>Ctenopharyngodon idella</i> (grass carp)	.. 12,000
<i>Cyprinus carpio</i> (common carp)	.. 9,000
<i>Hypophthalmichthys molitrix</i> (silver carp)	.. 8,000
<i>Ictalurus punctatus</i> (channel catfish)	.. 11,000
<i>Tilapia aurea</i>	.. 18,900
<i>T. nilotica</i>	.. 24,000
<i>T. mossambica</i>	.. 30,000
<i>Mugil cephalus</i> (grey mullet)	.. 14,500
<i>Chanos chanos</i> (milkfish)	.. 32,000

In practice, one is seldom able to measure concentrations of all ions in water. However, the ability of water to conduct an electrical current (conductivity) increases as salinity rises. A conductivity meter may be used to measure conductivity and the conductivity value allows an approximation of salinity. Many conductivity meters have a scale for reading salinity directly. Another method for obtaining the approximate salinity of a water is to measure the total dissolved solids concentration. A sample is filtered through a fine paper, a known volume is evaporated and the residue remaining is weighed. The weight of the residue in milligrams per litre is the total dissolved solids concentrations and this closely approximates the salinity. In brackishwater, salinity may be estimated from the chloride concentration by the following equation :

$$\text{Salinity in mg/litre} = 30 + (1.805) \text{ chloride in (mg/litre)}.$$

In practice, chloride concentrations (chlorinity) can be measured with refractometers or temperature corrected hydrometers.

The degree of salinity in water reflects geological and hydrological conditions. Surface waters in areas of high rainfall

where soils are continually leached usually have low salinity (10 to 250 mg/litre). In arid regions, evaporation exceeds precipitation and salinity increases as a result of evaporation. Salinity values in ponds of arid regions often range between 500 and 2,500 mg/litre and much higher values are often encountered. Even in areas of high rainfall, ground water from wells may sometimes have salinity values as high as those encountered in surface waters of arid regions. Seawater has a high salinity (35,000 mg/litre), so the salinity of brackishwater ponds reflects the degree of dilution of seawater and freshwater. High rates of evaporation in brackishwater ponds during periods of low rainfall may cause them to become excessively saline. Salinities in excess of 45,000 mg/litre are difficult for even marine species to tolerate.

1.4. *Turbidity and Colour*

The term turbid indicates that a water contains suspended material which interferes with the passage of light. In fish ponds, turbidity which results from planktonic organisms is a desirable trait, whereas that caused by suspended clay particles is undesirable. Even with the latter conditions, the clay particles are seldom abundant enough in water to directly harm fish. If the pond receives runoff which carries heavy loads of silt and clay, the silt settles over the pond bottom and smothers fish eggs and fish food organisms. The clay particles which remain in suspension restrict light penetration and limit the growth of plants. A persistent clay turbidity which restricts visibility into the water to 30 cm or less may prevent development of plankton blooms. Methods of controlling clay turbidity will be discussed later.

Some ponds receive large inputs of vegetative matter from their watershed. Extracts from this plant material (humates) often impart colour to the water. Colour from vegetative extracts often appears as a dark stain giving the water the appearance of tea or weak coffee. Pond waters with high concentrations of humates are typically quite acid and have a low total alkalinity. Although colour does not affect fish directly, it restricts light penetration and reduces plant growth. Agricultural

limestone applications have been used to successfully remove humates from natural waters.

1.5. Plankton

Plankton is comprised of all the microscopic organisms which are suspended in water and includes small plants (phytoplankton), small animals (zooplankton) and bacteria. When there is enough plankton in the water to discolour it and make it appear turbid, the water is said to contain a plankton 'bloom.' The phytoplankton uses inorganic salts, carbon dioxide, water and sunlight to produce its own food. The zooplankton feeds on living or dead plankton and other tiny particles or organic matter

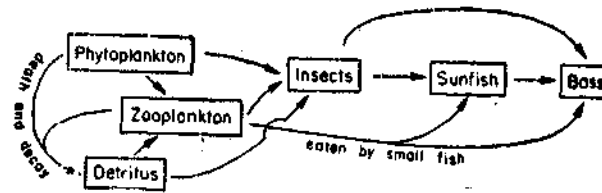


FIG. 1.2. A representative food web in a Sunfish-bass pond.

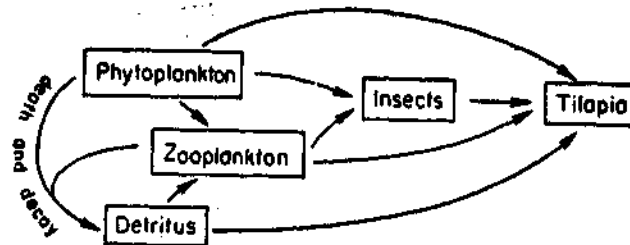


FIG. 1.3. A representative food web in a pond used for Tilapia culture.

in the water. Bacteria utilize any type of dead organic matter in the water for food. In fish culture systems where fish are not provided supplemental feed, plankton forms the most abundant base of the food web. Examples of food webs in fish culture systems are given in Figs. 1.2 and 1.3. Both food webs begin with phytoplankton growth. In Fig. 1.2 there are several steps before ending with largemouth bass, while in Fig. 1.3 the food

web is simpler because the Tilapia feed directly on plankton. Since each step in the food web is rather inefficient, a fish culture system with a more direct food web will produce a greater weight of fish per unit area. For example, during a 6 month period, the Sunfish-bass culture might produce 200 kg fish/ha while the Tilapia culture could easily produce 1,000 kg/ha.

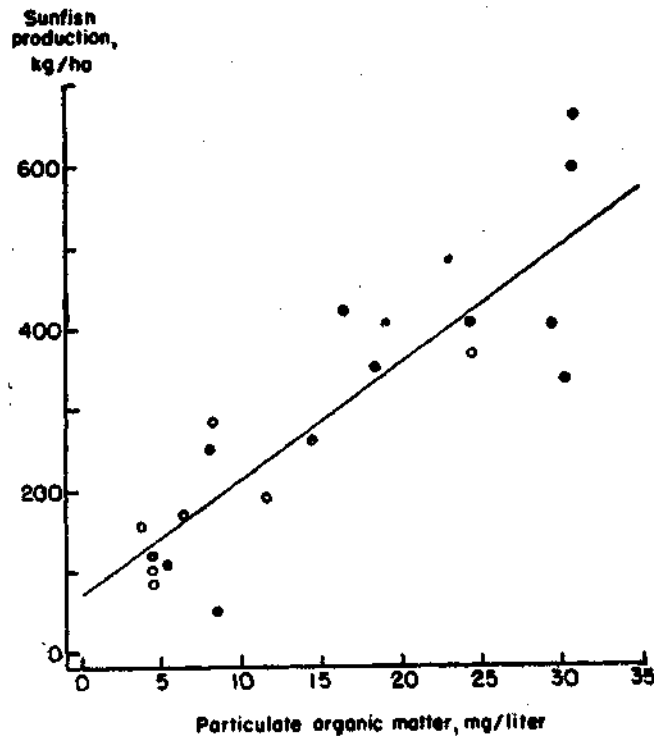


FIG. 1.4. Plankton production (particulate organic matter) and Sunfish production in ponds.

Because plankton is at the base of the food web, there is a close relationship between plankton abundance and fish production (Fig. 1.4). In addition to encouraging fish growth, plankton makes water turbid and prevents the growth of undesirable aquatic weeds through shading. Despite the benefits of plankton blooms in fish ponds, more plankton can sometimes be produced than can be utilized by the fish for growth. Heavy plankton

blooms usually contain large numbers of blue-green algae which can form scums at the surface. These scums absorb heat during the day and cause shallow thermal stratification. During the night, heavy plankton blooms consume large amount of dissolved oxygen and may cause oxygen depletion before the next morning. Scums of plankton may suddenly die, decompose and cause oxygen depletion. Relationships between plankton and dissolved oxygen will be treated more thoroughly later. In addition to causing dissolved oxygen problems, organisms in heavy plankton blooms often produce substances which impart a strong off-flavour to fish flesh.

There are several techniques for measuring the abundance or metabolic activity of the phytoplankton. The most popular are chlorophyll *a* determinations and measurements of primary productivity. A method for chlorophyll *a* is provided later. The total abundance of plankton is often ascertained from particulate organic matter analysis. Unfortunately, these techniques are too tedious for use in practical fish culture. The most practical technique for use in ponds which do not contain appreciable clay turbidity is to measure the Secchi disc visibility. Details for making Secchi disc measurements will be given later, but for now it will suffice to state that the Secchi disc visibility is the depth at which a disc 20 cm in diameter with alternative black and white quadrants disappears from view. There is a high correlation between Secchi disc visibility and plankton abundance, as illustrated in Fig. 1.5(1)*. It is impossible to establish an ideal plankton turbidity for fish culture. However, a Secchi disc visibility in the 30 to 60 cm range is generally adequate for good fish production and for shading underwater weeds. As Secchi disc visibilities decrease below 30 cm, there is an increase in the frequency of dissolved oxygen problems. At values above 60 cm, light penetrates to greater depths encouraging underwater macrophyte growth and there is less plankton to serve as food for fish or fish food organisms.

Plankton communities are constantly changing in species composition and in total abundance. This results in corresponding

* Number in parentheses indicates the reference in the Bibliography at the end of each chapter.

fluctuations in Secchi disc visibility and in the appearance of pond water. These changes in plankton communities may be disconcerting to the fish culturist. However, unless plankton becomes so dense that dissolved oxygen problems occur or so thin as to encourage underwater weeds, the changes do not affect fish

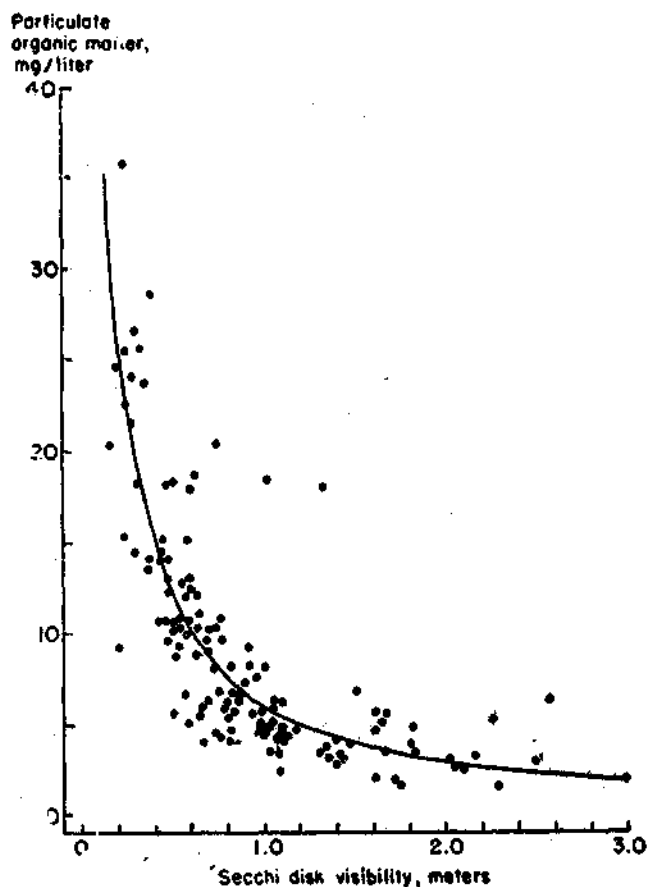


FIG. 1.5. Relationship between plankton abundance (particulate organic matter) and Secchi disc visibility in fish ponds.

production appreciably. By monitoring Secchi disc visibility on a regular schedule (once or twice weekly) and observing the appearance of the water, the fish culturist can obtain information on the continuing condition of the plankton community in a pond and on the supply of fish food organisms.

The ability of water to produce plankton depends on many factors, but the most important is usually the availability of inorganic nutrients for phytoplankton growth. Essential elements for phytoplankton growth include carbon, oxygen, hydrogen, phosphorus, nitrogen, sulphur, potassium, sodium, calcium, magnesium, iron, manganese, copper, zinc, boron, cobalt, chloride and possibly others. Phosphorus is most often the element regulating phytoplankton growth in ponds. The addition of phosphate fertilizer will cause an increase in plankton production and an increase in fish production in most ponds. Inadequate supplies of nitrogen, potassium and carbon also limit phytoplankton in some ponds. Nitrogen may be limiting in brackishwater and seawater ponds.

Even though the basic fertility of ponds differs greatly depending on the management and soils of their watersheds, the level of plankton production in most ponds can be raised within the range of plankton production needed for good fish production. Inorganic fertilizers may be added to ponds with low basic fertility to increase plankton production. In some ponds, both lime and fertilizer application may be required to increase plankton production. Manures also increase plankton production.

1.6. *Dissolved Oxygen*

Dissolved oxygen is probably the most critical water quality variable in fish culture, so the fish farmer should be familiar with the dynamics of dissolved oxygen concentrations in ponds. The atmosphere is a vast reservoir of oxygen, but atmospheric oxygen is only slightly soluble in water. The solubility of oxygen in freshwater at different temperatures and at standard sea level atmospheric pressure is given in Table 1.2. From this Table, it is readily apparent that the solubility of oxygen in water decreases as the temperature increases. When water contains a dissolved oxygen concentration equal to the solubility of oxygen in water at the existing temperature, the water is said to be saturated with dissolved oxygen. If water contains more dissolved oxygen than it should for the particular temperature, it is supersaturated. Water may also contain less dissolved oxygen than the saturation value. The solubility of dissolved oxygen decreases with

TABLE 1.2. *Solubility of dissolved oxygen in pure water at standard sea level Atmospheric pressure (1 atmosphere)*

°C	mg/litre	°C	mg/litre	°C	mg/litre
0	14.16	12	10.43	24	8.25
1	13.77	13	10.20	25	8.11
2	13.40	14	9.98	26	7.99
3	13.05	15	9.76	27	7.86
4	12.70	16	9.56	28	7.75
5	12.37	17	9.37	29	7.64
6	12.06	18	9.18	30	7.53
7	11.76	19	9.01	31	7.42
8	11.47	20	8.84	32	7.32
9	11.19	21	8.68	33	7.22
10	10.92	22	8.53	34	7.13
11	10.67	23	8.38	35	7.04

decreasing atmospheric pressure (barometric pressure). For example, the solubility of oxygen in water at 25°C differs as follows with altitude (given in milligrams per litre at specified altitudes): 0 m, 8.4 mg/litre; 500 m, 7.9 mg/litre; 1,000 m, 7.4 mg/litre; 1,500 m, 7.0 mg/litre; 2,000 m, 6.6 mg/litre; 2,500 m, 6.2 mg/litre; 3,000 m, 5.8 mg/litre. The solubility of oxygen in water also decreases as salinity increases. At temperatures of 20 to 35°C, the solubility of dissolved oxygen decreases by about 0.008 mg/litre for each 210 mg/litre increase in salinity. Thus, salinity is not an important factor regulating the concentration of oxygen in freshwater. Sea water has a high salinity and dissolved oxygen concentrations at saturation (Table 1.3) are considerably lower than for freshwater.

Even though dissolved oxygen will diffuse into water, its rate of diffusion is quite slow. Therefore, photosynthesis by phytoplankton is the primary source of dissolved oxygen in a fish culture system. Fish culturists are often concerned with the rate at which dissolved oxygen is removed from the water. The primary losses of dissolved oxygen from a pond include respiration by the plankton (phytoplankton include), respiration by fishes, respiration by benthic organisms (organisms living in or attached to the mud) and diffusion of oxygen into the air (7, 10). The

TABLE 1.3. *Solubility of dissolved oxygen in sea water at standard sea level atmospheric pressure (1 Atmosphere)*

°C	mg/litre	°C	mg/litre	°C	mg/litre
0	11.41	12	8.58	24	6.83
1	11.11	13	8.41	25	6.71
2	10.83	14	8.24	26	6.60
3	10.56	15	8.07	27	6.49
4	10.30	16	7.91	28	6.38
5	10.05	17	7.78	29	6.28
6	9.82	18	7.61	30	6.18
7	9.59	19	7.47	31	6.08
8	9.37	20	7.33	32	5.99
9	9.16	21	7.20	33	5.90
10	8.96	22	7.07	34	5.81
11	8.77	23	6.95	35	5.72

gains and losses of dissolved oxygen in a pond are summarised in Table 1.4 along with some values representing the usual magnitudes of daily gains and losses. It is readily apparent that plankton and fish respiration cause the major losses of dissolved oxygen and that photosynthesis is the largest source. Diffusion of oxygen into ponds only occurs when waters are below saturation and diffusion of oxygen out of ponds only occurs

TABLE 1.4. *Ranges of expected gains and losses of dissolved oxygen caused by different processes in fish ponds, for ponds of 1.0 to 1.5 metres average depth*

Process	Range mg/litre
<i>Gains</i>	
Photosynthesis by phytoplankton	5 to 20
Diffusion	1 to 5
<i>Losses</i>	
Plankton respiration	5 to 15
Fish respiration	2 to 6
Respiration by organisms in mud	1 to 3
Diffusion	1 to 5

when waters are supersaturated. The larger the difference between the dissolved oxygen concentration in the pond water and the concentration of dissolved oxygen at saturation, the greater is the rate of diffusion. Wind and wave action also favour diffusion.

In a fish culture system, more oxygen must enter or be produced in the water by plankton than is used by the organisms or dissolved oxygen depletion will occur. Since nutrients are normally abundant in well managed fish ponds, light is often the primary factor regulating photosynthesis by phytoplankton. Light rapidly decreases in intensity as it passes through water. This is true even in pure water, but the decrease is even faster in fish ponds because the planktonic organisms and other suspended and dissolved substances reflect and absorb light. Therefore, the rate of oxygen production by phytoplankton decreases with depth and below a certain depth, no more oxygen is produced. Since oxygen is continually used by the pond biota and only produced during daylight hours by the phytoplankton, there is a depth at which dissolved oxygen production by the phytoplankton and that entering by diffusion just equal the combined utilization of dissolved oxygen by pond life. Below this depth in stratified ponds the water will contain no dissolved oxygen. The stratification of dissolved oxygen in ponds usually corresponds closely to thermal stratification (3). The epilimnion contains dissolved oxygen and the hypolimnion is depleted of dissolved oxygen. As with thermal stratification daily dissolved oxygen stratification may occur in small shallow ponds.

Obviously, the depth to which light intensity is great enough for adequate photosynthesis to provide surplus dissolved oxygen is related to plankton density. Photosynthesis decreases with decreasing light intensity and as plankton becomes more abundant, the rate of oxygen consumption by the plankton community increases. When plankton abundance is great, dissolved oxygen production is extremely high near the surface. Because of shading, the rate of oxygen production will decrease rapidly with depth and only a thin layer of surface water, often less than 1 m will contain appreciable dissolved oxygen. In ponds where plankton is less abundant, rates of dissolved oxygen production are not as high within the illuminated layer of water, but there will be appreciable oxygen production and surplus dissolved

oxygen at greater depths than in ponds with greater plankton turbidity. The influence of plankton turbidity on the depth distribution of dissolved oxygen in ponds is illustrated in Fig. 1.6. As a general rule, most ponds will contain enough dissolved oxygen to support fish to a depth of at least two or three times the Secchi disc visibility.

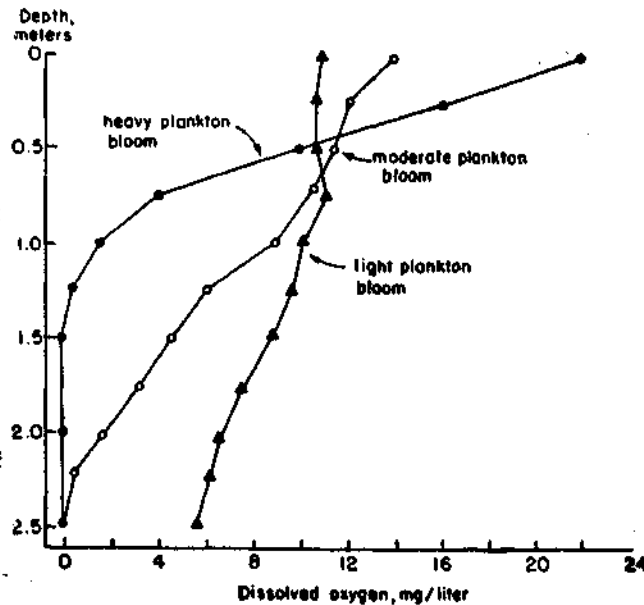


FIG. 1.6. Dissolved oxygen concentrations in the afternoon at different depths in ponds with different densities of plankton.

There is also a marked fluctuation in dissolved oxygen concentration during a 24 hour period in ponds. Concentrations of dissolved oxygen are lowest in the early morning just after sunrise, increase during daylight hours to a maximum in late afternoon and decrease again during the night. The magnitude of fluctuation is greatest in ponds with heavy plankton blooms and least in ponds with low plankton abundance. Daily fluctuations of dissolved oxygen concentrations in ponds with different plankton densities are depicted in Fig. 1.7. In ponds with extremely dense plankton blooms, dissolved oxygen concentrations will often be below 2 mg/litre in early morning. Concentrations are particularly low during periods of cloudy weather

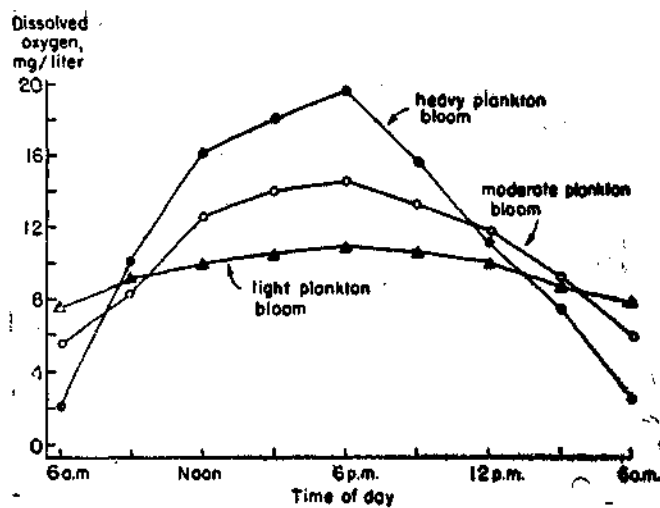


FIG. 1.7. Daily fluctuations in dissolved oxygen concentrations of surface water in ponds with different densities of plankton.

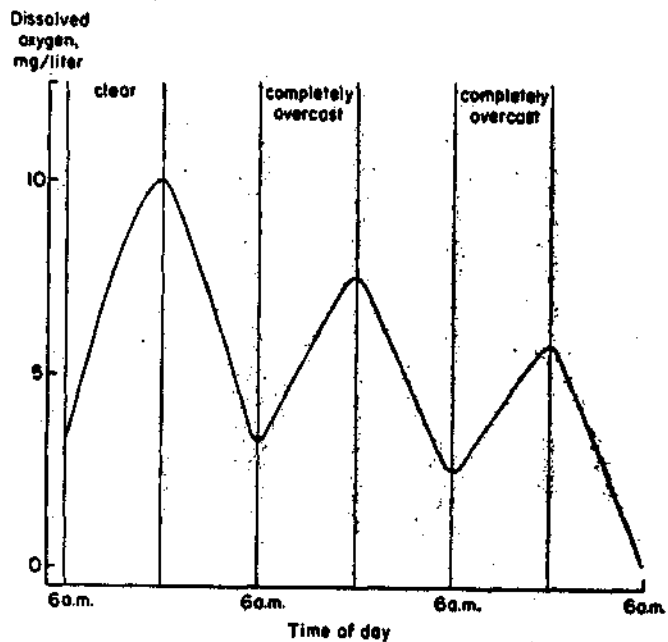


FIG. 1.8. Influence of cloudy weather on dissolved oxygen concentrations in fish ponds.

(5, 12). The production of oxygen on a cloudy day is less than on a clear or partly cloudy day, so dissolved oxygen concentrations do not increase to usual afternoon levels. This results in lower than usual dissolved oxygen concentrations the following morning. Extended periods of cloudy weather may result in dangerously low dissolved oxygen concentrations even in ponds with moderately heavy plankton blooms. The influence of cloudy weather on dissolved oxygen concentrations is illustrated in Fig. 1-8.

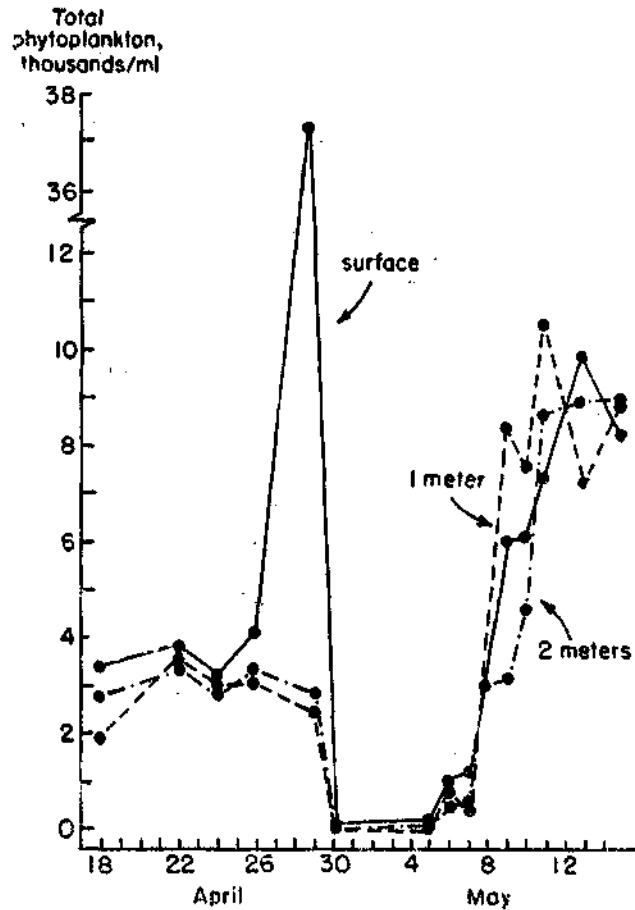


FIG. 1.9. Decline in phytoplankton following a phytoplankton die-off in a fish pond. The die-off began on April 29.

In ponds with heavy plankton blooms, scums of algae often form at the surface. Occasionally, the algae in these scums will suddenly die and their decomposition will result in depletion of dissolved oxygen (2, 6, 12). For example, Fig. 1-9 illustrates the sudden death of phytoplankton in a fish pond. The dissolved

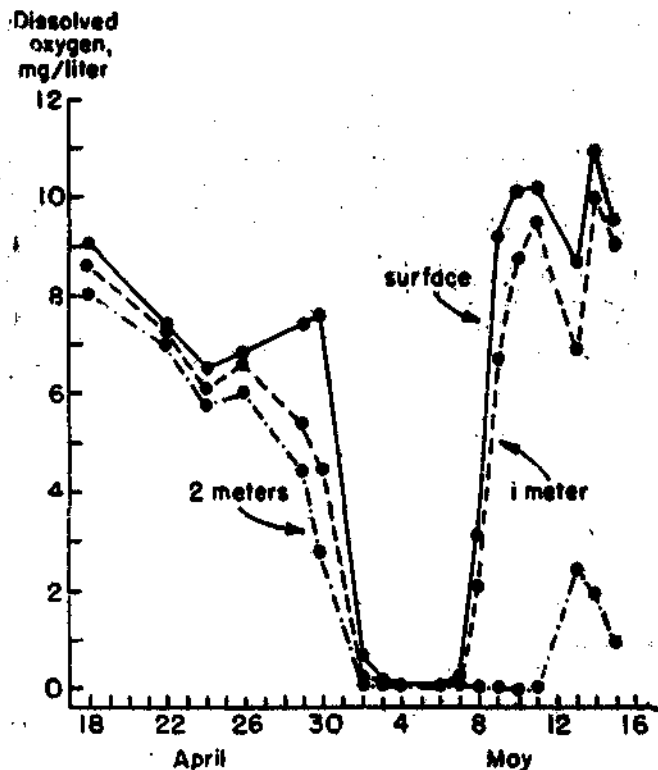


FIG. 1.10. Concentrations of dissolved oxygen before and after a phytoplankton die-off in a fish pond. The phytoplankton began dying on April 29.

oxygen concentration quickly dropped below a detectable level (Fig. 1.10). Dissolved oxygen concentrations did not return to normal levels until a new phytoplankton community was established (Figs. 1.9 and 1.10). Phytoplankton die-offs usually occur during calm, clear, warm weather. One can recognize a die-off because the algae scum deteriorates and the water takes on a brown or gray appearance.

Winds or heavy, cold rains may break up thermal stratification in ponds (12), causing complete mixing ('overturn') of oxygenless waters of the hypolimnion and the oxygenated water of the epilimnion. If the pond contains a large volume of oxygenless water, oxygen depletion may result.

Fish require adequate concentrations of dissolved oxygen for survival and growth. The minimum concentration for fish survival varies with time of exposure. A fish may tolerate a particularly low concentration of dissolved oxygen for a few hours without ill effect, but will die if exposed to this same concentration for several days. The concentration of dissolved oxygen tolerated by pond fishes is illustrated in Fig. 1.11, with additional data on oxygen requirements presented in Table 1.5. Low dissolved oxygen concentrations adversely affect fish even at levels which do not cause mortality, making them more susceptible to parasites and diseases (9). In addition, fish do not feed or grow as well when dissolved oxygen concentrations remain continuously below 4 or 5 mg/litre (5). Daily fluctuations of dissolved oxygen in fish ponds apparently have little effect on feeding and growth as long as the minimum dissolved oxygen concentration for the day does not drop below 1 or 2 mg/litre in the early morning and then rises near saturation within a few hours after sunrise. If dissolved oxygen concentrations remain at less than 3 or 4 mg/litre for prolonged periods, fish cease to feed or grow well.

TABLE 1.5. Reported lethal concentrations of dissolved oxygen for selected species of pond fish

Species	Lethal level (mg/litre)
<i>Carassius auratus</i> (goldfish)	.. 0.1 to 2.0
<i>Catla catla</i> (catla)	.. 0.7
<i>Cirrhina mrigala</i> (mrigal)	.. 0.7
<i>Ctenopharyngodon idella</i> (grass carp)	.. 0.2 to 0.6
<i>Cyprinus carpio</i> (common carp)	.. 0.2 to 0.8
<i>Hypophthalmichthys molitrix</i> (silver carp)	.. 0.3 to 1.1
<i>Labeo rohita</i> (rohu)	.. 0.7
<i>Ictalurus punctatus</i> (channel catfish)	.. 0.8 to 2.0
<i>Lepomis macrochirus</i> (bluegill)	.. 0.5 to 3.1
<i>Micropterus salmoides</i> (largemouth bass)	.. 0.9 to 3.1

1.7. pH

The pH is a measure of the hydrogen ion concentration and indicates whether the water is acidic or basic in reaction. The pH scale ranges from 0 to 14, with pH 7 being the neutral point. Thus, a water of pH of 7 is neither acidic nor basic, while a water with pH below 7 is acidic and one with a pH above 7 is basic. The greater the departure from pH 7, the more acidic or basic a water.

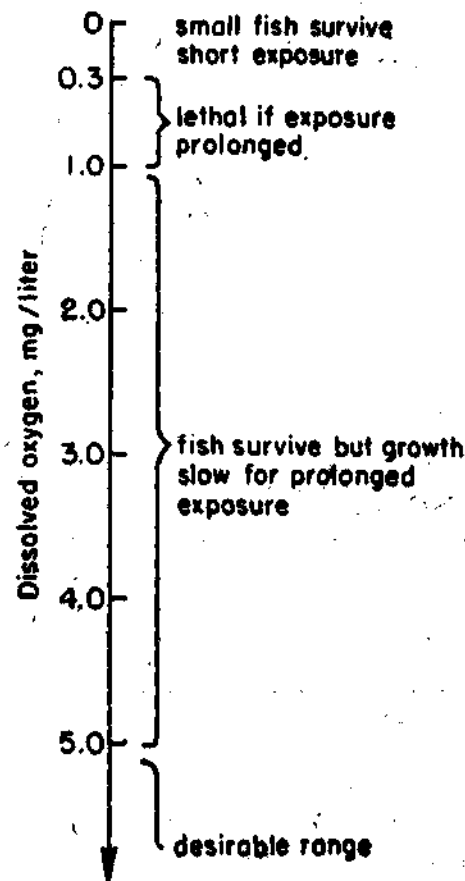


FIG. 1.11. Effects of dissolved oxygen concentrations on pond fish.

The pH of natural waters is greatly influenced by the concentration of carbon dioxide, an acidic substance. Phytoplankton

and other aquatic vegetation remove carbon dioxide from the water during photosynthesis, so the pH of a body of water rises during the day and decreases during the night (Fig. 1.12). Waters with low alkalinity often have pH values of 6 to 7.5 before daybreak, but when phytoplankton growth is heavy, afternoon pH values may rise to 10 or even higher (11). Fluctuations in pH are not as great in water with higher total alkalinity where pH values normally range from 7.5 or 8 at daybreak or 9 or 10 during the afternoon. In some water with extremely high total alkalinity and particularly in water with

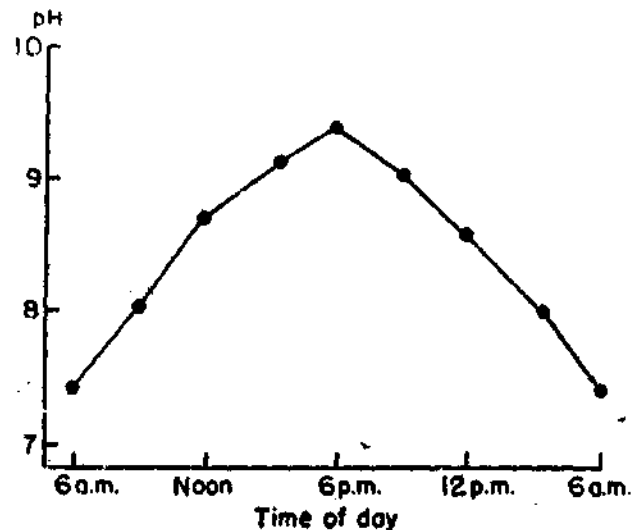


FIG. 1.12. Daily fluctuations in pH in a fish culture pond.

high total alkalinity and low total hardness, pH values may rise above 11 during periods of rapid photosynthesis (11). Obviously, pH measurements should be made in the early morning and again in the afternoon to assess the typical pH pattern for a pond. Waters with pH values of above 6.5 to 9 at daybreak are considered best for fish production. Some ponds which receive drainage from acid soils or swamps may be too acidic for fish production. Waters with extremely high total alkalinity may have pH values too high for fish culture. Methods for increasing or decreasing the pH of pond water will be given later.

The acid and alkaline death points for pond fish are approximately pH 4 and pH 11 respectively (11). Even though fish may survive, production will be poor in pond with early morning pH values between 4 and 6 and between 9 and 10 (Fig. 1.13). The afternoon pH in many fish culture systems rises to 9 or 10 for short periods without adverse effect on fish.

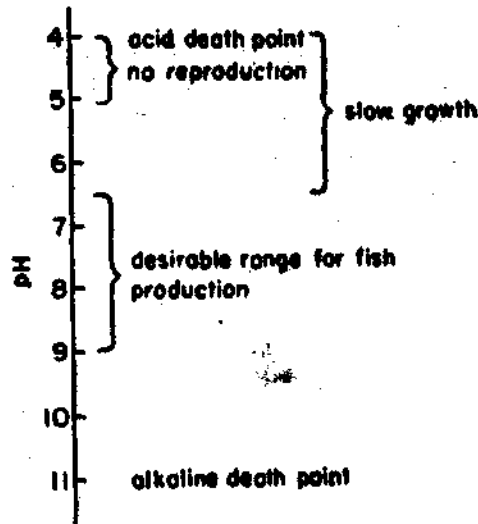


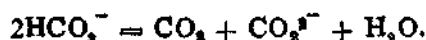
FIG. 1.13. Effect of pH on pond fish.

1.8. Carbon dioxide

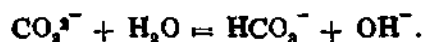
High concentrations of carbon dioxide can be tolerated by fish, although fish avoid levels as low as 5 mg/litre. Most species will survive in waters containing up to 60 mg/litre carbon dioxide, provided concentrations are high (8). When dissolved oxygen concentrations are low, the presence of appreciable carbon dioxide hinders the uptake of oxygen by the fish. Unfortunately, carbon dioxide concentrations are normally quite high when dissolved oxygen concentrations are low. This results because carbon dioxide is released in respiration and utilized in photosynthesis. When dissolved oxygen is low, photosynthesis is not proceeding rapidly. Therefore, carbon dioxide concentrations rise because carbon dioxide released by

respiration is not absorbed by phytoplankton for use in photosynthesis. Because of the relationship of carbon dioxide to respiration and photosynthesis, carbon dioxide concentrations usually increase during the night and decrease during the day. Particularly high concentrations of carbon dioxide occur in ponds after phytoplankton die-offs, after destruction of thermal stratification and during cloudy weather.

The influence of photosynthesis on pH is caused by carbon dioxide uptake according to the following equation :



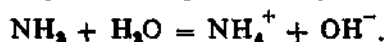
As plants remove carbon dioxide for use in photosynthesis, carbonate accumulates in the water. Carbonate hydrolyzes as follows :



The accumulation of hydroxide causes the pH to rise. At night, plants quit removing carbon dioxide and carbon dioxide from respiratory processes accumulates in the water. This causes the pH to drop because carbon dioxide, carbonate and water react to form bicarbonate. In other words, the reactions shown above go to the right during the day, but at night they go to the left.

1.9. Ammonia

Ammonia reaches pond water as a product of fish metabolism and decomposition of organic matter by bacteria. In water, ammonia nitrogen occurs in two forms, un-ionized ammonia and ammonium ion, in a pH and temperature dependent equilibrium :



As pH rises, un-ionized ammonia (NH_3) increases relative to ammonium ion. Temperature also causes an increase in the proportion of un-ionized ammonia, but the effect of increasing temperature is less than that of increasing pH. Percentages of un-ionized ammonia at different temperatures and pH values are given in Table 1.6. Analytical procedures for ammonia measure both un-ionized ammonia and ammonium ion (total ammonia nitrogen). The percentage un-ionized ammonia for the appropriate temperature and pH may be multiplied by the total ammonia nitrogen concentration to estimate the concentration of

un-ionized ammonia. For example, suppose the pH is 9.0, temperature is 28°C and total ammonia nitrogen is 1.0 mg/litre. The percentage un-ionized ammonia is 41.2% at pH 9 and 28°C; the un-ionized ammonia concentration is $1 \times 0.412 = 0.41$ mg/litre. The answer is in terms of ammonia-nitrogen; to convert to ammonia, multiple by the ratio 17/14 — the molecular weight of ammonia to the atomic weight of nitrogen.

TABLE 1.7. *Percentage un-ionized ammonia in aqueous solution at different pH values and temperatures*

pH	Temperature (°C)								
	16	18	20	22	24	26	28	30	32
7.0	0.30	0.34	0.40	0.46	0.52	0.60	0.70	0.81	0.95
7.2	0.47	0.54	0.63	0.72	0.82	0.95	1.10	1.27	1.50
7.4	0.74	0.86	0.99	1.14	1.30	1.50	1.73	2.00	2.36
7.6	1.17	1.35	1.56	1.79	2.05	2.35	2.72	3.13	3.69
7.8	1.84	2.12	2.45	2.80	3.21	3.68	4.24	4.88	5.72
8.0	2.88	3.32	3.83	4.37	4.99	5.71	6.55	7.52	8.77
8.2	4.49	5.16	5.94	6.76	7.68	8.75	10.00	11.41	13.22
8.4	6.93	7.94	9.09	10.30	11.65	13.20	14.98	16.96	19.46
8.6	10.56	12.03	13.68	15.40	17.28	19.42	21.83	24.45	27.68
8.8	15.76	17.82	20.08	22.38	24.88	27.64	30.68	33.90	37.76
9.0	22.87	25.57	28.47	31.37	34.42	37.71	41.23	44.84	49.02
9.2	31.97	35.25	38.69	42.01	45.41	48.96	52.65	56.30	60.38
9.4	42.68	46.32	50.00	53.45	56.86	60.33	63.79	67.12	70.72
9.6	54.14	57.77	61.31	64.54	67.63	70.67	73.63	76.39	79.29
9.8	65.17	68.43	71.53	74.25	76.81	79.25	81.57	83.68	85.85
10.0	74.78	77.46	79.92	82.05	84.00	85.82	87.52	89.05	90.58
10.2	82.45	84.48	86.32	87.87	89.27	90.56	91.75	92.80	93.84

As ammonia concentrations increase in the water, ammonia excretion by fish diminishes and levels of ammonia in blood and other tissue increases. The result is an elevation in blood pH and adverse effects on enzyme-catalyzed reactions and membrane stability. The permeability of the fish by water is affected and internal ion concentrations increase. Ammonia increases oxygen consumption by tissues, damages gills and reduces the ability of blood to transport oxygen. Histological changes occur in the gills, kidneys, spleen, thyroid and blood of fish exposed to sublethal concentrations of ammonia. Disease susceptibility also increases in fish exposed to sublethal concentrations of ammonia.

The tolerance of fish to ammonia varies with species, physiological condition and environmental conditions. Lethal concentrations for short-term exposure (24 to 72 hours) are between 0.4 and 2 mg/litre (5). Sublethal effects (histological changes) have been attributed to ammonia concentrations as low as 0.01 mg/litre. Ammonia concentrations as low as 0.06 mg/litre have slightly reduced growth in channel catfish; 0.52 mg/litre caused a 50% reduction in growth in this species; no growth occurred at 0.97 mg/litre.

It is difficult to evaluate ammonia concentrations in ponds because of the daily cycle in pH. Un-ionized ammonia may be quite high in the afternoon and negligible during the night.

1.10. Nitrite

When nitrite is absorbed by fish, it reacts with haemoglobin to form methemoglobin. Because methemoglobin is not an effective oxygen carrier, continued absorption of nitrite can lead to hypoxia and cyanosis. Blood containing methemoglobin is brown, so nitrite poisoning in fish is frequently called brown-blood disease.

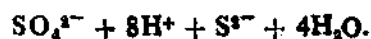
The sources of nitrite in fish ponds have not been definitely identified. However, the most likely source is the reduction of nitrate to nitrite in anaerobic muds. Regardless of the source, ponds occasionally contain nitrite concentrations of 0.5 to 10 mg/litre.

It is difficult to establish a lethal threshold value for nitrite, for its toxicity is related to water quality. Chloride and apparently calcium ions reduce the toxicity of nitrite to fish. As long as the molar ratio of chloride to nitrite does not drop below 3, channel catfish are not harmed by nitrite. Hence, sodium chloride application may be used to prevent brown-blood disease when nitrite concentrations are high. Calcium chloride is more effective than sodium chloride in alleviating nitrite toxicity in trout and salmon. Thus, the toxic level for nitrite varies with chloride and possibly calcium concentrations. Of course, a given level of nitrite in a particular water results in a specific percentage of methemoglobin in fish. However, the percentage of

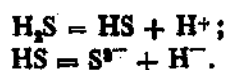
methemoglobin that is necessary to harm fish will differ with dissolved oxygen concentration. There is also evidence that the toxicity of nitrite increases with decreasing pH. Nitrite concentrations above 1 mg/litre in pond water are usually considered undesirable unless chloride concentrations are several milligrams per litre.

1.11. Hydrogen sulphide

Under anaerobic conditions, certain heterotrophic bacteria can use sulfate and other oxidized sulfur compounds as terminal electron acceptors in metabolism and excrete sulphide as illustrated below :



The sulphide excreted is an ionization product of hydrogen sulphide and participates in the following equilibria :



The pH regulates the distribution of total reduced sulfur among its forms. Un-ionized hydrogen sulfide is toxic to fish, but the ions resulting from its dissociation are not appreciably toxic. Analytical procedures measure total sulphide ; values given below show the percentage of un-ionized hydrogen sulfide at different pH values :

pH	Hydrogen sulphide (%)
5.0	99.0
5.5	97.0
6.0	91.1
6.5	76.4
7.0	50.6
7.5	24.4
8.0	9.3
8.5	3.1
9.0	1.0

Concentrations of hydrogen sulphide of 0.01 to 0.05 mg/litre are lethal to fish and any detectable concentration of hydrogen

sulphide in pond water is considered undesirable. Obviously, if the pH of a water can be increased by liming, the toxicity of hydrogen sulphide will decrease.

1.12. *Total alkalinity and total hardness*

The term total alkalinity refers to the total concentration of bases in water expressed as milligrams per litre of equivalent calcium carbonate. In natural waters, these base are primarily carbonate and bicarbonate ions. Another way to think of alkalinity is in terms of basicity and resistance to pH change. The amount of acid required to cause a specified change in pH in a given volume of water increases as a function of the total alkalinity levels of the waters. In general, early morning pH is greater in waters with moderate or high total alkalinity than in waters with low total alkalinity. The availability of carbon dioxide for phytoplankton growth is related to alkalinity. Waters with total alkalinities less than 15 or 20 mg/litre usually contain relatively little available carbon dioxide. Waters with total alkalinities of 20 to 150 mg/litre contain suitable quantities of carbon dioxide to permit plankton production for fish culture. Carbon dioxide is often in low supply in waters with more than 200 to 250 mg/litre of total alkalinity. The afternoon pH in waters with low total alkalinity may often be as great as in waters with moderate or high total alkalinity. Waters of low alkalinity are poorly buffered against pH change and the removal of carbon dioxide results in rapidly rising pH.

The total concentration of divalent metal ions (primarily calcium and magnesium) expressed in milligrams per litre of equivalent calcium carbonate is termed the total hardness of water. Total alkalinity and total hardness values are normally similar in magnitude because calcium, magnesium, bicarbonate, and carbonate ions in water are derived in equivalent quantities from the solution of limestone in geological deposits. However, in some waters total alkalinity may exceed total hardness and vice versa. If total alkalinity is high and total hardness low, pH may rise to extremely high levels during periods of rapid photosynthesis.

Desirable levels of total hardness and total alkalinity for fish culture generally fall within the range of 20 to 300 mg/litre.

If total alkalinity and total hardness are too low, they may be raised by liming. However, there is generally no practical way of decreasing total alkalinity and total hardness when they are above the desirable level. As a general rule, the most productive waters for fish culture have total hardness and total alkalinity values of approximately the same magnitude. For example, a water with a total alkalinity of 150 mg/litre and a total hardness of 25 mg/litre is not as good for fish culture as a water in which the total alkalinity is 150 mg/litre and the total hardness is 135 mg/litre.

1.13. *Aquatic weeds*

Large aquatic plants (aquatic macrophytes) which may grow in fish ponds are usually undesirable. They interfere with fish management operations such as seining, feeding and fish harvest, compete with phytoplankton for nutrients, provide havens for prey fish to escape predatory fish and thus encourage unbalanced fish populations, favour mosquito production and contribute to water loss through evapotranspiration. Aquatic macrophytes include filamentous algae and submerged, floating-leafed, floating and emergent macrophytes. Aquatic macrophytes which being their growth at the pond bottom are limited to relatively transparent waters. Therefore, management procedures which favour plankton turbidity will often eliminate macrophytes(13). Obviously, floating or floating-leafed macrophytes must be controlled by other methods.

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FISH FEEDING AND WATER QUALITY

Fish eat most of the feed applied to ponds, but on a dry matter basis, only a small percentage of the chemical substances in feed are converted to fish flesh. To illustrate, in channel catfish culture, feed conversion values (weight feed applied/weight fish produced) are about 1.5. Thus, if 3,000 kg of feed were provided to fish in a 1-ha pond, 2,000 kg of fish could be expected. However, the fish are about 25% dry matter and the feed is about 92% dry matter. Thus, 2,760 kg of dry matter in feed might result in 500 kg of dry matter in fish — a dry matter conversion ratio of 5.52. The difference between dry matter in feed and in fish, 2,260 kg represents chemical substances that reach the water in metabolic wastes. The wastes includes carbon dioxide, ammonia, phosphate and other organic and inorganic substance.

Nutrients from metabolic wastes stimulate phytoplankton. In a catfish pond receiving upto 50 kg/ha of feed per day (1), the metabolic waste from the production of 1 kg of live catfish resulted in 2.69 kg of dry weight of organic matter in phytoplankton. Furthermore, fish excrete ammonia, each kg of live catfish resulted in 0.061 kg of ammonia (1). Thus, as feeding rates increase, phytoplankton density and ammonia concentration increase in fish ponds. For example, at feeding rate of 50 kg/ha/day, chlorophyll *a* concentrations averaged 45 µg/litre in catfish ponds; at 100 kg/ha/day of feed, chlorophyll *a* averaged 75 µg/litre. Of course, peak chlorophyll *a* concentrations were much greater — 150 and 250 µg/litre respectively, at feeding rates of 50 and 100 kg/ha/day. Total ammonia nitrogen averaged 0.5 mg/litre at 50 kg/ha/day of feed and 0.9 mg/litre at 100 kg/ha/day. Of course, peak concentrations were higher.

The density of phytoplankton during the course of a growing season is also related to feeding rate. For example, as the feeding rate was gradually increased in a catfish pond,

phytoplankton abundance increased as evident from a decrease in Secchi disc visibility (Fig. 2.1).

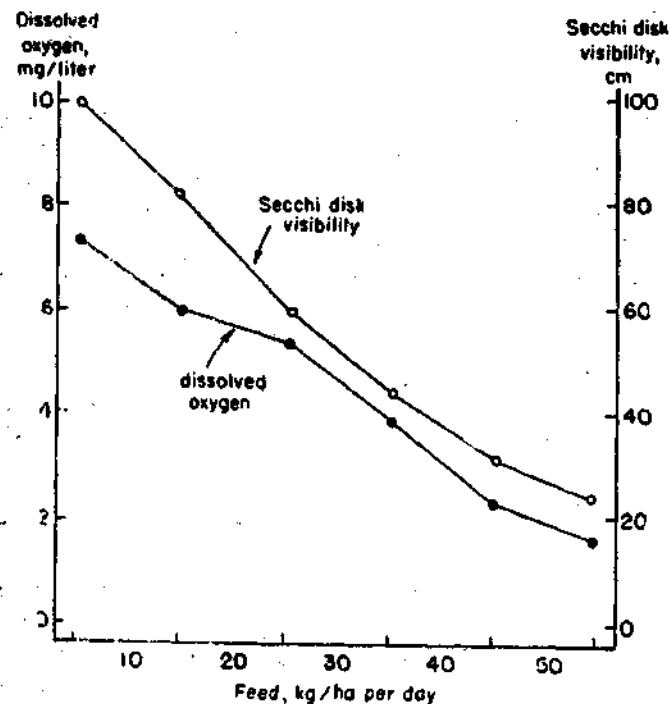


FIG. 2.1. Secchi disk visibilities and early morning (0630 hrs.) dissolved oxygen concentrations in a channel catfish pond as the feeding rate was gradually increased from May to September.

As phytoplankton density increases with feeding rate, there is a decrease in the early morning dissolved oxygen concentration (Fig. 2.1). In ponds stocked at different rates with channel catfish (3), there was good agreement between feeding rates, Secchi disk visibility (phytoplankton abundance) and early morning dissolved oxygen concentrations (Table 2.1). If feeding rate continues to increase, a level is reached where phytoplankton abundance is so great that dissolved oxygen depletion may occur each night. Without aeration, fish cannot survive at very high feeding rates. Of course, even with aeration and adequate dissolved oxygen concentrations, feeding rates may become so high that high ammonia concentrations limit fish production.

As feeding rates increase, fish production increases. However, because ammonia concentration increase and dissolved oxygen concentrations during the night decrease, conditions for fish production gradually decline as feeding rates increase. For example, at feeding rates of 34, 56, 78 and 92 kg/ha of feed per day, feed conversion values for channel catfish in ponds were 1.3, 1.7, 2.5 and 6.3 respectively. Hence, as feeding rates and fish production increase in un-aerated ponds, the amount of feed required to produce a given weight of fish increases. Because of the diminishing returns from feed, a point is reached where applying more feed becomes uneconomical.

TABLE 2.1. *Average early morning dissolved oxygen concentrations and Secchi disc visibilities in channel Catfish ponds with different feeding rates*

Feeding rate	Early morning dissolved oxygen (mg/litre)	Secchi disc visibility (cm)
Low (34 kg/ha/day)	4.71	68
Medium (56 kg/ha/day)	2.95	45
High (78 kg/ha/day)	1.95	21

In aerated ponds, feed conversion values were essentially constant (1.3 to 1.8) between feeding rate values of 25 and 125 kg/ha/day. At 150 kg/ha of feed, the feed conversion value was 3.0. At 200 kg/ha of feed per day, the feed conversion value was over 15. Dissolved oxygen concentrations were adequate in all ponds and the increase in feed conversion values at high feeding rates was attributed to high ammonia concentrations.

The ultimate limit on feeding rate and fish production is set by water quality. As a general rule, fish production increases linearly with feeding rate while water quality deteriorates exponentially with feeding rate.

Odours and flavours described as 'earthy-musty' are often detected in fish from ponds. These odour and flavours originate

from organic substances that are synthesised and excreted into the water by blue-green algae and actinomycetes. The substances are absorbed by fish and impart an 'off-flavour' to fish flesh. Off-flavour is an important problem in the commercial culture of fish, for off-flavour fish may not be suitable for market. The environmental factors that favour off-flavour in pond fish are not understood. However, the problem is worse during warm weather and in ponds with high feeding rates (2). Many techniques for preventing off-flavour in pond fish have been tried, but none have been successful in all cases. At present, the only known means of immediately removing off-flavour from fish is to hold the fish in fresh water for several days. This technique is usually impractical. Fortunately, off-flavour problems usually disappear from pond within a few weeks to a few months. Many times, through the necessity to hold fish for an indeterminable period while off-flavour disappears is an inconvenience and added cost to fish farmers.

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4.1. *Introduction*

Phytoplankton growth in waters with low alkalinity is often limited by inadequate carbon dioxide and bicarbonate ion. Some waters of low alkalinity are so acid that fish do not survive or grow well. Muds in ponds with low total alkalinity are acid and strongly absorb the phosphorus added in fertilizer. The addition of a liming material increases the pH of bottom muds and makes phosphorus more available. Liming also increases the availability of carbon for photosynthesis by raising the total alkalinity of the water. The greater total alkalinity after liming results in a higher concentration of bicarbonate ion which is in equilibrium with carbon dioxide. Liming also increases the pH and total hardness of pond waters. Ponds with total alkalinity values less than 10 mg/litre seldom produce adequate plankton for good fish production unless they are limed. Responses to fertilization are variable in unlimed ponds with waters containing 10 to 20 mg/litre total alkalinity, but unlimed ponds with waters above 20 mg/litre total alkalinity consistently, produce adequate plankton after fertilization to allow good fish production provided all other factors are favourable (5).

The decision to lime a pond should always be based upon total alkalinity measurements rather than guesswork. Ponds in same general area may differ greatly in total alkalinity. For example, most ponds near Auburn, U.S.A. will benefit from liming, but among these ponds are a few which have total alkalinity values well above 20 mg/litre. The "rule of thumb" recommendation that all ponds in the vicinity of Auburn, Alabama need lime would result in unnecessary and wasteful application of lime to some ponds. In determining whether or not to lime a pond, one should recognize that there is no single total alkalinity value below which lime is undoubtedly needed. Experience has shown that liming is of little or no

benefit if total alkalinity is above 20 mg/litre. At total alkalinity values below 20 mg/litre, judgment must be used to decide whether or not to lime because the need for lime increases with decreasing total alkalinity. In ponds with total alkalinity values between 15 and 20 mg/litre, the response to liming may be too slight to justify the effort and expense. One should not use lime in a pond if fertilization is not to be employed because liming alone will not appreciably increase fish production except in waters that are so acid that fish will not survive or grow at normal rates. Furthermore, lime is seldom needed in ponds where fish are supplied feed and do not depend upon naturally occurring organisms for food.

4.2. *Lime requirement*

When lime is applied to a pond, it reacts with the mud and until enough lime is added to satisfy the lime requirement of the mud, little if any of the added lime will be available to increase the pH, total alkalinity and total hardness. A lime requirement procedure is available for determining the amount of lime needed to raise the total alkalinity above 20 mg/litre in ponds (2, 4). A simplified lime requirement technique is provided in Chapter 7. This procedure is based upon a chemical analysis of a mud sample and many fish culturists and biologists will be unable to obtain a lime requirement value for their pond. In this event, liming material equivalent to about 2,000 kg/ha of calcium carbonate may be applied and the total alkalinity determined after 1 or 2 months. If the total alkalinity is still too low, another application equal in amount to the first should be made and the total alkalinity measured again. This procedure should be repeated until enough lime has been applied to maintain the total alkalinity above 20 mg/litre. The addition of liming material equal to about 2,000 to 6,000 kg/ha of calcium carbonate should suffice for most ponds. However, some ponds which have high concentrations of organic matter in bottom muds or have sulphide deposits in bottom muds or on their watersheds may require much greater amounts of lime. Occasionally the lime application rate may be so high that cost of the lime will be prohibitive and the water will be unsuited for fish culture.

Typical effects of liming may be illustrated by results of experiments conducted at Auburn University (1). Agricultural limestone (finely crushed dolomite) was applied to five ponds at the rate of 4,000 kg/ha and five ponds served as the unlimed controls. All ten ponds were fertilized. Liming caused a

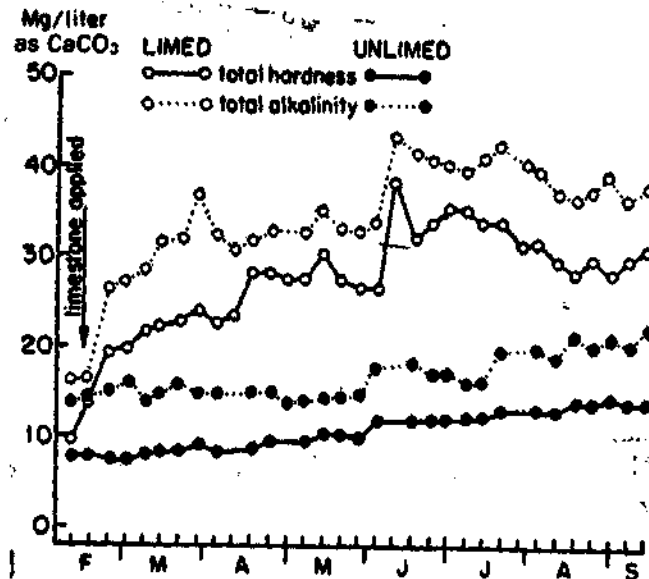


FIG. 4.1. Effect of application of agricultural limestone on total hardness and total alkalinity in fish ponds.

marked increase in total hardness and total alkalinity (Fig. 4.1). The pH of bottom muds increased in the limed ponds (Table 4.1). The production of Tilapia was 25% greater in the limed ponds than in the control ponds. The total alkalinity of

TABLE 4.1. Average mud pH values for five limed and five unlimed ponds — lime applied between February 17 and March 17, 1983

Type pond	November	August	January
	1972	1973	1974
Limed	5.2	6.7	6.8
Unlimed	5.4	5.5	5.5

these ponds before liming averaged 13.5 mg/litre. Even greater responses to liming have been reported in waters which had lower total alkalinity before liming.

4.3. *Applying lime to ponds*

Agricultural limestone is the best liming material to use in ponds. The material should be finely ground (particles should pass through a sieve with 0.025 cm openings) and have a high neutralizing value. Small particle size is necessary so that the agricultural limestone will react quickly with water and mud. The neutralizing values of liming materials refer to the amounts of acid they will neutralize, expressed as a percentage of the amount of acid neutralized by an equal amount of pure calcium carbonate (3). A method for determining neutralizing value is provided in Chapter 7. Thus, pure calcium carbonate has a neutralizing value of 100% and is used as a standard in referring to liming rates. In other words, if one wants to apply a liming material at a rate equal to 2,000 kg/ha of calcium carbonate and the liming material has a neutralizing value of 80%, he should apply 2,500 kg/ha ($2,000 \text{ kg} \div 0.80$) of the liming material.

Hydrated lime [calcium hydroxide, $\text{Ca}(\text{OH})_2$] and burnt lime (calcium oxide, CaO) have higher neutralizing values than agricultural limestone, but if applied in large quantities, hydrated lime and burnt lime cause excessively high pH and fish mortality. Hydrated lime and burnt lime are sometimes applied to waters which contain no fish or to muds of ponds which have been drained to raise the pH and kill fish disease organisms. Basic slag has been used as a liming material in fish culture, but its neutralizing value is lower than that of most agricultural limestones and extremely large applications of basic slag are required. Agricultural gypsum (calcium sulphate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is not a liming material, although it has incorrectly been used as one by some fish culturists.

Liming materials can be easily broadcast over the bottoms of empty ponds, but application is more difficult when ponds are full of water. Best results may be achieved by broadcasting the liming material over the entire pond surface. Bags

of liming material may be emptied from a moving boat. Bulk liming material is cheaper and may be applied from a plywood platform attached between two boats. Liming materials should be applied during the late fall or early winter in temperate regions so that it will react with waters and muds before fertilizers are applied in the spring. In tropical regions, lime should be applied at least 1 month before fertilizer applications are initiated. This is important because liming materials will precipitate phosphorus if applied at or near the same time as fertilizers. However, once the liming material has reacted with the mud, greater availability of phosphorus fertilizer will result. The residual effect of liming is governed by the rate of water loss to seepage and pond overflow. In ponds with normal rates of water loss, liming will usually last for 3 to 5 years. Once a pond has been limed, small annual applications (20% to 25 % of the initial application rate) may be used to avoid having to make large applications of lime every few years.

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5

DISSOLVED OXYGEN AND AERATION

5.1. *Introduction*

Almost all problems with dissolved oxygen in fish culture are the consequences of heavy plankton blooms. In fertilized ponds, fertilization should be halted when plankton blooms get too dense (i.e., Secchi disc readings of 25 cm or less). In ponds where fish are supplied feeds, heavy plankton blooms are the natural consequences of high feeding rates. Lower feeding rates will result in less plankton growth, but only at the expense of decreased fish production. Suitable plankton densities result in Secchi disc visibilities of 30 to 60 cm. The probability of problems with low dissolved oxygen concentration increases as the magnitude of the Secchi disc visibility decreases below 30 cm. In ponds with Secchi disc visibility values of 10 to 20 cm, dissolved oxygen concentrations may fall so low at night that fish are stressed and a cloudy day may lead to dissolved oxygen depletion before the next morning. Aeration is an effective means of preventing fish mortality when dissolved oxygen is low and aeration can be used to permit high levels of fish production.

5.2. *Management of dissolved oxygen*

A number of procedures are used to prevent fish kills when dissolved oxygen concentrations are dangerously low. Application of upto 6 or 8 mg/litre of potassium permanganate has been frequently recommended in the United States. The potassium permanganate is supposed to oxidize organic matter and lower the demand for dissolved oxygen in the pond. Recent research at Auburn University has demonstrated that potassium permanganate is entirely worthless for this purpose and that its application actually increases the length of time required for dissolved oxygen concentrations to return to normal levels. Applications of calcium hydroxide have been recommended to

destroy organic matter in ponds with low dissolved oxygen concentrations and thereby reduce rates of oxygen consumption by bacteria. There is no reason to believe that applications of calcium hydroxide will lower concentrations of organic matter. However, when dissolved oxygen is low, carbon dioxide is usually quite high. The application of calcium hydroxide will remove carbon dioxide which will allow fish to better utilize the low concentration of dissolved oxygen. Each milligram per litre of carbon dioxide will require 0.84 mg/litre of calcium hydroxide for its removal. For example, if a pond contains 25 mg/litre of carbon dioxide, a calcium hydroxide treatment of 21 mg/litre ($25 \text{ mg/litre} \times 0.84$) would remove the carbon dioxide. Following phytoplankton die-offs, applications of fertilizers have been employed to encourage phytoplankton growth and foster dissolved oxygen production. Research to document the effectiveness of this procedure has not been conducted, but nutrient concentrations are already high in ponds following phytoplankton die-offs and it is doubtful that fertilization is necessary.

The only really effective procedure for preventing fish mortality during periods of extremely low dissolved oxygen involves the use of mechanical devices. Large, tractor-powered pumps may be used to pump fresh, oxygenated water from a nearby pond into the pond with low dissolved oxygen concentrations. Alternatively, water from wells, spring, streams, etc. may be released into the oxygen depleted pond. Well water should be discharged across a baffle for aeration because well water is often high in carbon dioxide and deficient in dissolved oxygen. When oxygenated water is released into a pond with oxygen depletion, bottom water which contains less dissolved oxygen and more carbon dioxide than surface water should simultaneously be released from the pond if possible. Pumps may also be used to pump water from the pond with low dissolved oxygen and release this water with force back onto the surface of the same pond. The agitation and circulation of the water increases its dissolved oxygen content. However, this method is not as effective as pumping fresh, oxygenated water from another pond or well into the pond with low dissolved oxygen. Various types of aeration devices may be used to introduce oxygen into waters with low dissolved oxygen

concentrations. Small spray-type surface aerators are in common use. These aerators are most effective in small ponds or when several are operated in a large pond. More powerful aerators such as the Crisafulli pump and sprayer and the paddle-wheel aerator supply considerably more dissolved oxygen to ponds than the spray-type surface aerators. However, Crisafulli pumps and paddle-wheel aerators are expensive and must be operated from the power take-off of a farm tractor. Large fish farms and research stations can afford to maintain and operate emergency aeration equipment, but small scale fish culturists have little recourse when faced with dissolved oxygen problems. Fortunately, problems with dissolved oxygen seldom occur except in ponds where fish are fed at high rates.

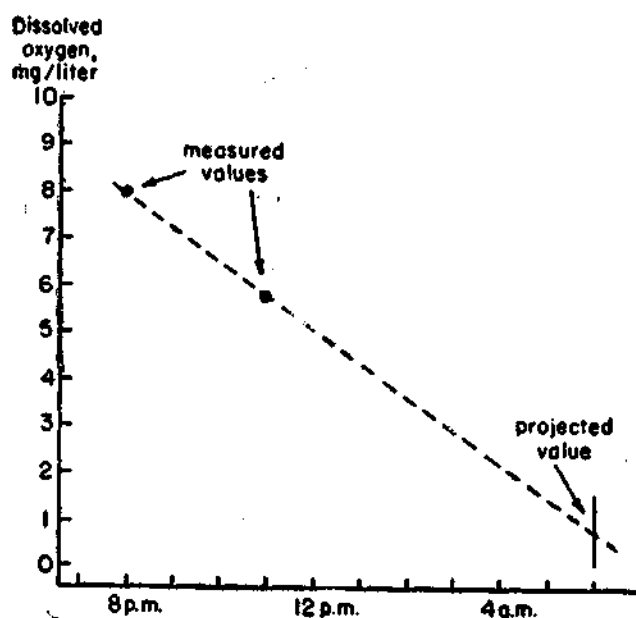


FIG. 5.1. A graphical method for predicting the night time decline in dissolved oxygen concentration in fish ponds.

Fish culturists often monitor dissolved oxygen concentrations during the night in ponds to determine if emergency aeration is needed. Recent research has resulted in procedures for predicting how low dissolved oxygen concentrations will fall during

the night. Such predictions permit the fish culturist to prepare for emergency aeration in advance. The simplest of these procedures involves the measurement of dissolved oxygen concentrations at dusk and two or three hours later. These two values are plotted versus time on a graph and a straight line is projected through the two points and used to estimate the dissolved oxygen concentration at later hours during the night. The use of this technique is illustrated in Fig. 5.1.

5.3. *Aeration and fish production*

Continuous or night time aeration can increase production of catfish in ponds, as results of four studies summarized below clearly demonstrate.

Loyacano (5) aerated white catfish ponds with a blower that forced air through openings in pipes on pond bottoms. Because of improved water quality, higher feeding rates were employed in aerated ponds. Three ponds aerated at 10.5 m³ of air/minute/ha had average net fish production of 5,500 kg/ha. Average net fish production for three unaerated ponds was 2,700 kg/ha.

Parker (7) used air-lift pumps for aeration and obtained a maximum harvest weight of 15,800 kg of channel catfish/ha and unaerated ponds yielded 3,000 kg/ha. Of course, stocking and feeding rates were much higher in aerated ponds. In spite of aeration with air-lift pumps, low dissolved oxygen (DO) in some ponds necessitated additional aeration with splash-type surface aerators. Parker also flushed one volume of water through ponds every two weeks.

Plemmons (8) employed continuous aeration with splash-type surface aerators at 5.5 kw/ha. Unaerated ponds stocked at 12,200 channel catfish/ha had an average harvest weight of 2,500 kg/ha. Aerated ponds stocked at 30,100 fish/ha yielded 12,800 kg of catfish/ha. Plemmons occasionally employed emergency aeration with a Crisafulli pump to prevent DO depletion even though ponds were continuously aerated with small surface aerators. He also flushed appreciable water through some ponds in hopes of improving water quality.

Hollerman and Boyd (4) (stocked channel catfish at 19,770/ha in 12 ponds. Six ponds were aerated for two to six hours per night with splash-type aerators at 5.5 kw/ha and six ponds were not aerated. Emergency aeration and water exchange were not employed. Fish kills were common in unaerated ponds, but rare in aerated ponds. Harvest weights averaged 1,400 kg/ha in unaerated ponds and 5,390 kg/ha in aerated ponds.

In all four cases summarised above, the increase in fish production was attributed to higher concentrations of DO resulting from aeration. The studies also demonstrated that aeration will not always prevent DO depletion. Stocking, feeding rates and oxygen demands were higher in aerated ponds. At times, demands for oxygen exceeded abilities of small aerators to supply oxygen and emergency aeration with larger aerators and water exchange was employed to prevent fish kills. Economic analyses of data collected by Parker (7), Plemmons (8) and Hollerman and Boyd (4) suggested that aeration could increase profits. However, it is difficult to extrapolate economic data from small research ponds to actual fish-farm conditions.

Benefits of aeration have been clearly illustrated in research. However, because of a lack of understanding of the principles of aeration and of aerator function, fish farmers often fail to achieve the maximum benefits of aeration. Therefore, some basic facts are provided below about aerators and aeration.

5.4. *Oxygen transfer*

At a specified combination of water temperature, salinity and atmospheric pressure, water contains a given concentration of oxygen at equilibrium (saturation). For freshwater fish ponds in the southeastern United States, temperature is the major factor causing differences in DO concentrations in saturated waters. If the DO concentration is below saturation, oxygen will diffuse from the air into the water until saturation is finally attained. The driving force causing net movement of oxygen from air to water is the oxygen saturation deficit (DO at saturation minus actual DO concentration). The greater the saturation deficit, the faster oxygen will enter the water.

Oxygen must enter the water through the surface film, but if the DO concentration in a body of water is to rise, oxygen entering the film must be mixed throughout the water column. Water in the film quickly increases in DO concentration, but unless the oxygen-enriched water in the film is mixed with underlying water of lower DO concentration, the rate of diffusion of oxygen into the surface film will be greatly retarded. The movement of oxygen through still water is slow, so turbulence is necessary to maintain a large oxygen saturation deficit between surface film and air. Turbulence (mixing) continuously replaces oxygen-enriched water in the surface film with water of lower DO concentration.

The rate of diffusion of oxygen into water depends primarily upon the oxygen saturation deficit, the ratio of water surface to water volume and the degree of turbulence. In a given body of water, natural aeration is largely a function of the saturation deficit and wind velocity. Waves increase the surface to volume ratio and turbulence mixes surface water with underlying water. Aerators also provide oxygenation by increasing the area of contact between air and water and the amount of turbulence.

5.5. *Types of aerators*

Aerators increase the area of contact between air and water by (a) agitating surface water, (b) releasing air bubbles beneath the surface or (c) both. While oxygenating water, aerators also impart energy to water and cause horizontal and vertical mixing. Flexibility in aerator design permits many types of aerators, a few of which are described below.

Diffused-air aerators employ an air blower or air compressor and porous pipe to release air bubbles at the pond bottom (Fig. 5.2). The efficiency of oxygen transfer is related to bubble size — small bubbles offer a greater air-water interface than do large bubbles. Water depth also influences efficiency, because the deeper the bubbles are released, the greater the contact time between bubbles and water.

Venturi aerator suck air into water so that bubbles are formed (Fig. 5.3). The aspirating-propeller-pump aerator is a modifica-

tion of the venturi aerator in which a propeller at the end of a hollow shaft imparts velocity to water and sucks air down the shaft. This air is mixed into the turbulent water as fine bubbles.

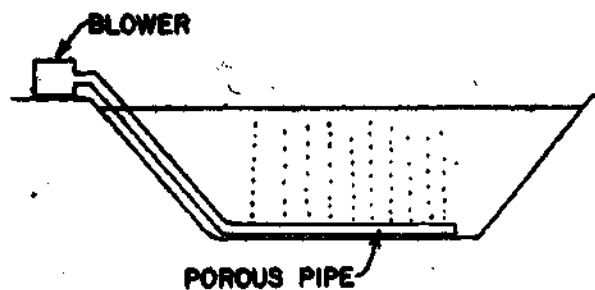


FIG. 5.2. Diffused-air aeration.

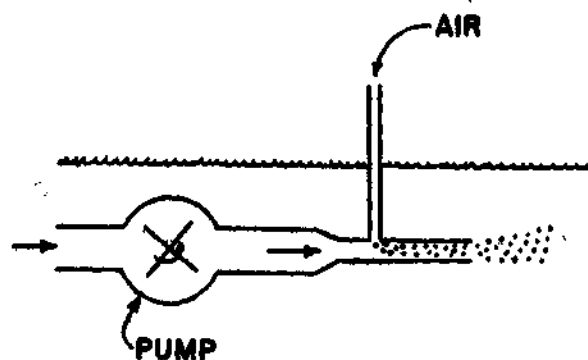


FIG. 5.3. Venturi aerator.

U-tube aerators (10) are usually 12 to 18 m deep (Fig. 5.4), hence bubbles have a long contact time with water. Unless adequate head is available, water must be pumped through the U-tube.

An air-lift pump (Fig. 5.5) consists of an open-ended pipe or tube into which air is released. The air bubbles rise through the tube and effect oxygenation. Of course, the movement of bubbles through the pipe results in pumping of water.

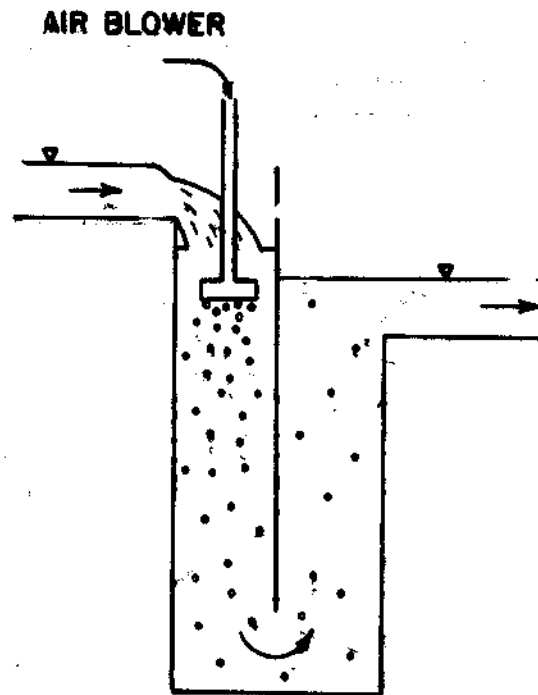


FIG. 5.4. U-tube aerator.

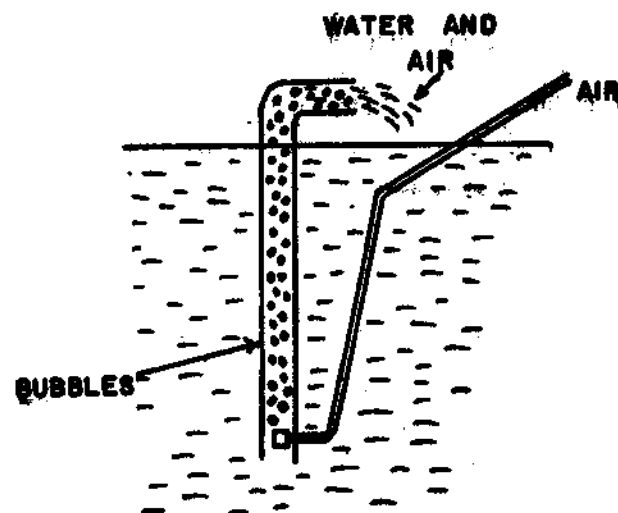


FIG. 5.5. Airlift pump aerator.

Splasher-type surface aerators (vertical turbines) jet water into the air (Fig. 5.6). Water is broken into turbulent, thin layers and drops that have large surface-to-volume ratios. Paddle-wheel aerators are another common type of surface aerator.

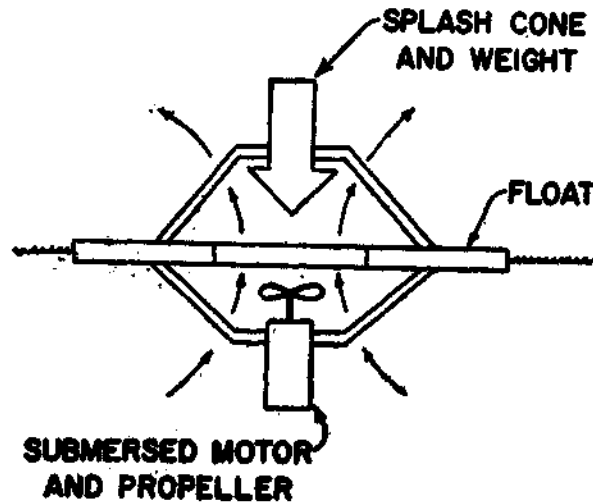


FIG. 5.6. Splasher-type surface aerator.

Gravity aerators employ head loss. Water falls over a weir or from a pipe onto a splash board (Fig. 5.7), paddle-wheel, brush or inclined plane. Water may be pumped to the top of a vertical pipe and allowed to fall through perforated aprons.

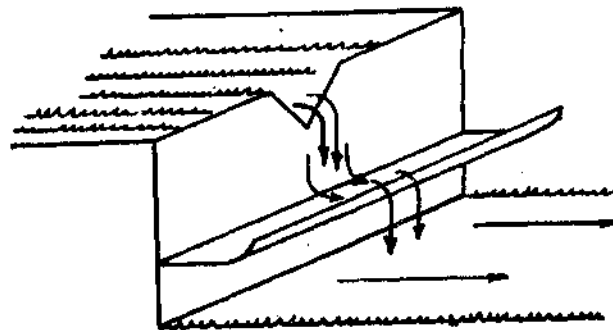


FIG. 5.7. Gravity-flow aeration using a splash board.

Chesness and Stephens (2) demonstrated that all gravity aerators mentioned above were effective in oxygenating water.

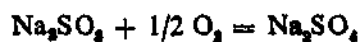
Colt and Tchobanoglous (3) presented standard oxygen transfer rates for various types of aerator (Table 5.1). With the exception of the highly efficient U-tube aerator, all aerator had oxygen transfer rates of 0.6 to 2.4 kg oxygen/kw/hour. The U-tube aerator is highly efficient, but is difficult and expensive to construct and has virtually no application in pond fish culture.

TABLE 5.1. Typical rates of oxygen transfer under standard conditions for aeration systems used in fish culture (3)

Aeration system	Transfer rate (Kg oxygen/Kw/ hour)
Diffused-air systems	
Fine bubble	.. 1.2—2.0
Medium bubble	.. 1.0—1.58
Coarse bubble	.. 0.6—1.2
Low-speed surface aeration (with or without draft tube)	1.2—2.4
High-speed floating aerator	.. 1.2—2.4
U-tube aerator	.. 4.5—45.6
Gravity aerator	.. 1.2—1.8
Venturi aerator	.. 1.2—2.4
Static tube systems	.. 1.2—1.6

5.6. Testing aerators

Aerators are tested in small basins — often 200,000 litres or less. A basin is filled with clean tap water and DO is removed with sodium sulphite and cobalt chloride. Sodium sulphite reacts with oxygen as follows :



Theoretically, 7.9 mg/litre of sodium sulphite are needed to remove 1 mg/litre of DO. However, because the aerator is used to mix the sodium sulphite, some oxidation of sulphite occurs during the mixing period. About 1.5 times the theoretical quantity of sodium sulphite normally is added. Cobalt chloride serves as a catalyst — it is applied at 0.05 to 0.1 mg/litre of cobalt. Once the water is deoxygenated, the aerator is operated to raise

the oxygen concentration in the basin. Measurements of DO are made at intervals (a minimum of six to ten times while the DO rises from 0 to 70 or 80 % of saturation) at different locations (at least four to six locations) in the basin. The plot of the natural logarithm of the saturation deficit versus time should give a straight line, the slope of which is the oxygen transfer coefficient (K_{La}). The K_{La} is calculated by the equation

$$K_{La} = \frac{\ln (C_s - C_1) - \ln (C_s - C_2)}{t_2 - t_1}$$

where

K_{La} = oxygen transfer coefficient in hr^{-1} ;

C_s = DO concentration at saturation in mg/litre ;

C_1 = initial DO concentration in mg/litre ;

C_2 = final DO concentration in mg/litre ;

t_1 = time that DO concentration reaches 10 or 20 % of saturation (C_1) in mg/litre ;

t_2 = time that DO concentration reaches 70 or 80 % of saturation (C_2) in mg/litre.

The K_{La} calculated by the above equation is for the temperature of water in the test basin. By convention, K_{La} values are corrected to 20°C [$(K_{La})_{20}$]:

$$(K_{La})_T = (K_{La})_{20} \times 1.024^{T-20}$$

where

T = temperature of water in the test basin in °C.

The amount oxygen transferred per hour at standard conditions (tap water ; 20°C ; 0 mg/litre DO) may be obtained by

$$(OT)_{20} = (K_{La})_{20} \times C_{20} \times V \times 10^{-6}$$

where

$(OT)_{20}$ = oxygen transfer in kg/hr under standard conditions (tap water, 20°C, 0 mg/litre DO) ;

C_{20} = DO concentration at saturation and 20°C in mg/litre ;

V = Volume of test basin in litres.

Additional information on aerator tests are presented by the American Public Health Association *et al.* (1) and Stuckenberg *et al.* (11).

5.7. Oxygen transfer in ponds

Pond conditions are different from those in test basins and oxygen-transfer rates for ponds are less than those obtained in test basins and reported by manufacturers. Nevertheless, oxygen transfer ratings are useful in comparing the capabilities of different aerators.

If pond waters are saturated with oxygen, aerators cannot transfer more oxygen. However, the further below saturation the DO, the more efficiently aerators transfer oxygen and the greatest efficiency is for 0 mg/litre DO. Aerators are rated for 20°C and pond waters are usually warmer. The rate of oxygenation of tap water is usually greater than that of pond water and tap water often holds more DO at saturation than does pond water of the same temperature. The following equations are used in obtaining factors for relating aeration of tap water to aeration of pond water (12):

$$\alpha = \frac{(K_L a)_{20} \text{ Pond water}}{(K_L a)_{20} \text{ Tap water}}$$

$$\beta = \frac{C_{20} \text{ Pond water}}{C_{20} \text{ Tap water}}$$

Shelton and Boyd (9) determined α and β values for 43 samples of pond water. The β factors ranged from 0.92 to 1.00 and the mean standard deviation was 0.98 ± 0.019 . Values for 84% of the ponds were between 0.96 and 1.00. The α factors for the 43 samples ranged from 0.66 to 1.07 with a mean of 0.94 and a standard deviation of ± 0.084 . Most of the pond waters had factors between 0.90 and 1.00. Alpha factors greater than 1.0 are not uncommon because waters may contain natural surfactants that enhance oxygen transfer. Most factors for fish ponds were somewhat larger than those for wastewater.

The following equation (6) corrects standard oxygen-transfer rates for pond conditions:

$$(OT)_p = OT_{20} \left[\frac{(\beta C_s - C_p)}{9.07} (1.024)^{T-20} \alpha \right]$$

where

$(OT)_p$ = oxygen transfer rate under pond conditions in kg O_2 /kw/hr ;

$(OT)_{30}$ = manufacturer's rating in kg O_2 /kw/hr ;

C_p = DO Concentration in pond in mg/litre.

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MISCELLANEOUS TREATMENTS AND CALCULATION OF TREATMENT RATES

6.1. *Introduction*

Three miscellaneous treatments for improving water quality in ponds are covered in this chapter. These include turbidity removal, aquatic plant control and pH reduction. Information for calculating treatment rates is also provided.

6.2. *Removal of clay turbidity*

In some ponds, it is necessary to remove the turbidity caused by suspended clay particles so that light will penetrate deep enough into the pond for phytoplankton growth. The oldest technique for removing clay turbidity involves the application of organic matter (3, 5). Recommendations vary, but the most popular include: two or three applications of 2,000 kg/ha of barnyard manure; one or more applications of 2,000 to 4,000 kg/ha of hay; and 75 kg of cottonseed meal plus 25 kg of superphosphate per hectare at 2 to 3 week intervals. The effectiveness of organic matter applications in removing clay turbidity varies and several weeks must usually pass before one can determine if a particular treatment was a success.

A better method for removal of clay turbidity is treatment with filter alum (aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$). Alum will cause suspended clay particles to coagulate and precipitate from the water within a few hours (1). The exact application rate for alum may be determined by treating samples of pond water in beakers with concentration of alum ranging from 10 to 40 mg/litre at 5 mg/litre concentrations intervals. The lowest concentration of alum which causes a floc of clay particles to form within 1 hour is taken as the desired treatment rate. Many fish culturist will be unable to conduct this test, but an application of 25 to 30 mg/litre will apparently precipitate the clay turbidity from most ponds. When applying alum it should

be dissolved in water and quickly distributed, preferably by spraying, over the entire pond surface. Application should be made during calm, dry weather because mixing by wind and rain will break up the floc and prevent it from settling out. The results of alum treatment in four ponds are illustrated in Table 6-1.

TABLE 6.1. *Effects of alum (Aluminium Sulphate) treatment on clay turbidity in fish ponds*

Pond	Alum applied (mg/litre)	Turbidity units		Reduction in turbidity (%)
		Before treatment	After treatment	
E-67 ..	15	40	2	95
E-68 ..	20	28	3	89
E-73 ..	20	19	3	84
S-27 ..	20	830	24	97

Alum has an acid reaction in water, so it destroys total alkalinity and reduces pH. Each milligram per liter of alum will decrease the total alkalinity by 0.5 mg/liter. If the total alkalinity of water is below 20 mg/litre, alum treatment may depress the pH to the point that fish are adversely affected. Hydrated lime (calcium hydroxide, $\text{Ca}(\text{OH})_2$) applied simultaneously at the rate of 0.40 mg/litre for each 1.0 mg/litre increment of alum will prevent unfavourable changes in alkalinity and pH. Another alternative is to lime ponds that have waters of low alkalinity before treating with alum. Liming materials will often precipitate clay turbidity, but if turbidity persists after liming, alum treatment may be conducted without danger of pH depression.

Although alum treatment will clear pond water of clay turbidity, it does nothing to correct the cause of turbidity. Unless the source of the turbidity is eliminated, ponds will again become turbid with clay particles. Clay turbidity usually results because ponds receive large volumes of turbid runoff after each rain. Erosion of the watershed may be prevented by revegetation. If this is impossible, it is sometimes possible to divert the turbid runoff from the pond by use of a diversion ditch.

6.3. *Reduction of pH*

Waters which have high total alkalinities and low total hardnesses may have dangerously high pH values during periods of rapid phytoplankton growth. Waters of this type do not occur often, but one should analyse the water to determine if the potential for high pH exists.

Liming to increase total hardness is of no value in preventing high pH because lime application increases total alkalinity and total hardness by roughly the same amount. Applications of ammonium fertilizers have been recommended to lower the pH of pond water. The ammonium ion in fertilizer is nitrified to nitrate with the release of hydrogen ion which lowers the pH. However, at high pH a large percentage of the ammonium ion applied to a pond will immediately be transformed to un-ionized ammonia which is highly toxic to fish. Filter alum (aluminium sulphate) may be added to ponds to decrease pH. An alum treatment equal in milligrams per litre to the phenolphthalein alkalinity will reduce the pH to approximately 8.5. Although alum treatment may be used to prevent a fish kill when the pH is too high, it does nothing to change the conditions responsible for high pH.

Agricultural gypsum (calcium sulphate) may be applied to water to increase the total hardness without affecting the total alkalinity. Experience indicates that gypsum will alleviate the conditions responsible for high pH, but confirmatory research is needed. The best treatment rate for agricultural gypsum appears to be the amount which will increase the total hardness to a level where it equals the total alkalinity. The treatment rate may be determined from the following equation :

Agricultural

$$\text{gypsum (mg/litre)} = (\text{Total alkalinity} - \text{Total hardness}) \times 2.2$$

The agricultural gypsum should be applied in the same manner as liming materials. The residual effect of gypsum treatment is not known.

6.4. *Aquatic plant control*

As mentioned earlier, one effective technique of controlling many species of macrophytes is through fertilization to produce plankton turbidity and shade the pond bottom. This technique is especially powerful if ponds are constructed so that no areas are shallower than about 60 cm. Grass carp (white amur) eat tremendous quantities of aquatic vegetation and provide a biological method for controlling macrophytes. When stocked at 60 to 80 per hectare, grass carp will control most species of macrophytes that cannot be controlled by plankton turbidity. Grass carp are even effective in controlling macrophytes in ponds that are not turbid with plankton. In small ponds, macrophytes may be controlled by cutting or by dragging them out with a rake or seine.

Herbicides are also used in fish culture to control macrophytes. The manufacturer's label gives the rate and method of application for a herbicide. The label provides information on safety precautions. Usually the concentrations of aquatic herbicides used to kill macrophytes are safe to fish. Decay of macrophytes killed by herbicides can cause dissolved oxygen depletion. If ponds have extensive areas of macrophytes, 1/4 to 1/5 portions of the pond should be treated at 1 to 2 week intervals to reduce the chance of dissolved oxygen depletion. The major limitation of herbicides for controlling macrophytes is that once the concentration of a herbicide declines to a non-toxic level, macrophytes will regrow. Thus, repeated applications of herbicides are required to control macrophytes, often at considerable expense.

Algicides are sometimes used to control phytoplankton in ponds. Copper sulphate, the most widely used algicide, will kill most species of phytoplankton at concentrations of 0.1 to 0.5 mg/litre in waters with total alkalinities below 40 to 50 mg/litre (6). In waters with higher alkalinities, copper sulphate concentrations of 1.0 mg/litre or more may be required to kill phytoplankton. Copper sulphate may be applied by dissolving it in water and distributing it over the pond surface. Alternatively, copper sulphate crystals may be placed in a burlap bag and the bag

towed behind about until the copper sulphate dissolves. Burlap bags of copper sulphate may be positioned in ponds so that the chemical gradually dissolves and mixes with the water (2). Copper sulphate may also be used to treat scums of phytoplankton which drift to the leeward sides of ponds (4).

Phytoplankton killed by copper sulphate decomposes rapidly and may result in low dissolved oxygen concentrations. Copper sulphate has no appreciable residual toxicity and phytoplankton growth will resume soon after treatment. Fish are susceptible to copper sulphate and in waters with alkalinities less than 20 mg/litre, treatment with 0.5 to 1.0 mg/litre of copper sulphate may kill fish.

Synthetic algicides such as Diuron (3-(3, 4-dichlorophenyl)-1, 1-dimethyl urea) and Simazine (2-chloro-4, 6-bis (ethylamino), s-triazine) are sometimes used to kill phytoplankton. These algicides are extremely toxic to algae, have a long residual action and are not toxic to fish at concentrations used to kill phytoplankton. As with copper sulphate, extensive mortality of phytoplankton following applications of synthetic algicides may result in depletion of dissolved oxygen. Some fish culturists have attempted to 'thin' phytoplankton blooms by small, periodic applications of synthetic algicides to ponds receiving heavy applications of feed. However, recent research (7) demonstrated that this practice results in prolonged periods of low dissolved oxygen concentrations and reduced fish yields.

6.5. Calculating treatment rates

Concentrations for chemical treatments of ponds are given in milligrams per litre so fish culturists must calculate how much of a chemical to add to a pond to give the desired concentration. To calculate the amount of a chemical needed, the volume of the pond must be known. Assuming the surface area of a pond is known, the simplest technique for obtaining the average depth to use in computing the volume is to make transects (8 or 10 will usually suffice) across the pond in a boat while making depth soundings at regular intervals with a calibrated rod or sounding line. The average of all soundings is taken as the average depth.

Once the volume of a pond is known, it is a simple matter to calculate treatment rates. Since 1 cubic metre (m^3) weighs 1,000 kg and 1 gram contains 1,000 mg, then 1 gram per l m^3 equals 1 mg/litre. The following examples illustrate how to calculate amounts of chemicals to add to ponds.

Example : A pond has a surface area of 0.26 ha and an average depth of 1.15 m. How much filter alum (100% pure) must be applied to the pond to give an alum concentration of 25 mg/litre ?

- (1) Since $0.26 \text{ ha} = 2,600 \text{ m}^2$, the pond volume is
 $2,600 \text{ m}^2 \times 1.15 \text{ m} = 2,990 \text{ m}^3$.

(2) Each cubic metre will require 25 g of alum for a concentration of 25 mg/litre, so the amount of alum needed for the entire pond is

$$2,990 \text{ m}^3 \times 25 \text{ g/m}^3 = 74,750 \text{ g}.$$

- (3) A treatment of 74,750 g equals 74.75 kg.

Example : The average depth of a pond is 0.57 m and the surface area is 0.01 ha. How much agricultural gypsum (8% pure) must be applied to produce a gypsum concentration of 50 mg/litre ?

- (1) Since $0.01 \text{ ha} = 100 \text{ m}^2$, the pond volume is
 $100 \text{ m}^2 \times 0.57 \text{ m} = 57 \text{ m}^3$.

(2) Each cubic metre will require 50 g of gypsum for a concentration of 50 mg/litre, but the agricultural gypsum is only 80% pure. Therefore, we may calculate the concentration of gypsum as follows :

$$50 \text{ g} \div 0.80 = 62.5 \text{ g}.$$

The amount of agricultural gypsum needed for the entire pond will be

$$57 \text{ m}^3 \times 62.5 \text{ g/m}^3 = 3,562 \text{ g or } 3.56 \text{ kg}.$$

Example : A pond with a volume of $1,000 \text{ m}^3$ must be treated with a herbicide. The herbicide is a liquid with 75% active ingredient and a density of 0.85 g/ml (0.85 kg/litre). How much of the liquid herbicide must be applied to the pond to give a concentration of 1 mg/litre of active ingredient ?

(1) The amount of the active ingredient to give a concentration of 1 mg/litre is

$$1000 \text{ m}^3 \times 1 \text{ g/m}^3 \times 1000 \text{ g} = 1.0 \text{ kg.}$$

(2) The herbicide has an active ingredient content of 75%, so the weight of herbicide containing 1.0 kg active ingredient is

$$1.0 \text{ kg} \div 0.75 = 1.33 \text{ kg.}$$

(3) The density of the herbicide is 0.85 kg/litre, so the volume of the herbicide weighing 1.33 kg is

$$1.33 \text{ kg} \div 0.85 \text{ kg/litre} = 1.56 \text{ litres.}$$

Thus, 1.56 litres of the liquid herbicide would give a concentration of 1 mg/litre of the active ingredient when applied to the pond.

6.6. *Applying chemicals to pond*

Chemicals which are applied to ponds come in a variety of formulation including crystals, solutions, soluble powders, emulsifiable concentrates and granules. Fish culture stations and large fish farms can afford rather elaborate equipment for applying chemicals. For example, chemicals may be dissolved in a tank of water or some other solvent and sprayed over the surface with a power sprayer. Liquids may be dispersed uniformly from a boat mounted tank through a boom consisting of a pipe with a series of small diameter holes in its underside. A valve regulates the rate at which the solution is fed by gravity into the water or a pump may be used to effect more uniform and forceful release. Dispensers for granules or powder may consist of hoppers with adjustable dispensing holes in the bottom. An auger is employed to prevent clogging of holes. Finally, chemicals may be released into the wash of an outboard motor propeller to effect mixing as the boat moves over the pond surface.

In instances where the owner of one or a few ponds must apply chemicals, it is usually not practical to purchase or construct an elaborate dispenser. The chemical can be dissolved or mixed in a large container of water and applied to the pond surface. Application may be accomplished with a pressurized

garden sprayer. However, if sprayer is not available the solution or mixture may be splashed with dipper over the pond surface. Care should be taken to dispense the chemical as uniformly as possible. Granules may be broadcast by hand or with a small 'cyclone' seeder. Crystals may be placed in a burlap bag and the bag towed behind a boat until they have dissolved. Only a little ingenuity is needed to develop a method for applying a chemical to a pond once the treatment rate has been established.

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WATER ANALYSIS

The purpose of this chapter is to present methods of water and mud analysis that are frequently employed in fish culture. These include Secchi disc visibility, pH, total alkalinity, total hardness, dissolved oxygen, carbon dioxide, chemical oxygen demand, ammonia, nitrite, chlorophyll *a*, particulate organic matter, hydrogen sulphide and lime requirement of muds. Also included is a method for neutralizing value of limestone.

WATER SAMPLING

Water samples for dissolved oxygen or carbon dioxide analysis must be collected so that they do not come in contact with air.

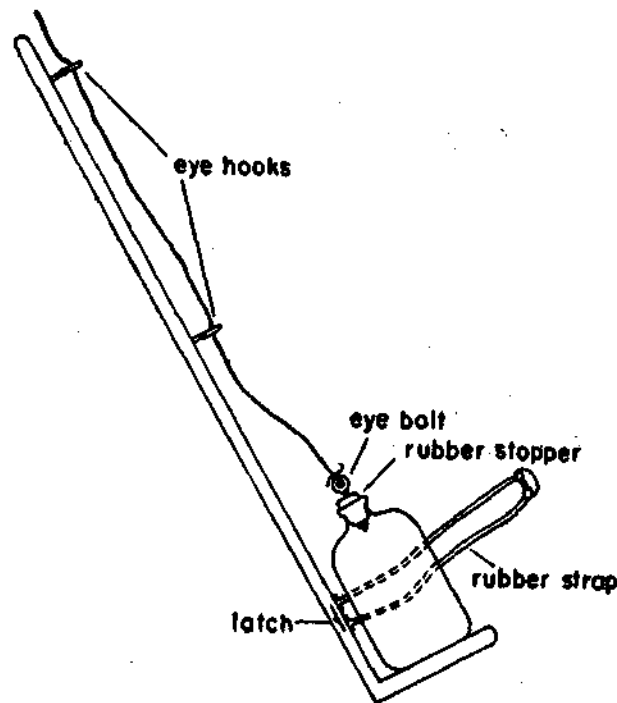


FIG. 7.1. Water sampler useful for collecting water from depths of up to 2 m.

Van Dorn, Kemmerer or sewage samplers, which may be purchased from scientific supply houses, are most commonly employed for taking samples for dissolved gas analysis. Samples for other variables may be dipped from the surface with open containers. Samplers may be constructed from inexpensive materials for securing samples from greater depths (Figs. 7.1 and 7.2). Of course, water collected with samplers of the types shown in Figs. 7.1 and 7.2 would be contaminated with air and unfit for dissolved oxygen or carbon dioxide analysis.

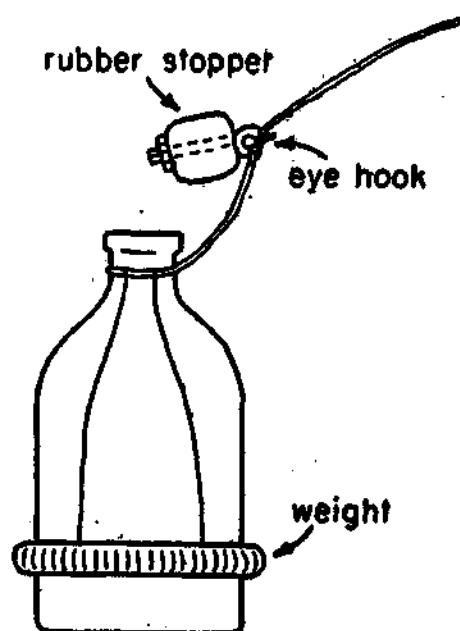


FIG. 7.2. A weighted bottle water sampler.

SECCHI DISC VISIBILITY

A Secchi disc is 20 cm in diameter, painted with black and white quadrants and attached to a calibrated line (Fig. 7.3). The disc is weighted on the underside with a lead plate so that it will sink readily. Secchi discs may be purchased from scientific supply houses or constructed from sheet metal, plexiglass or masonite. A flat paint should be used to prevent glare. A

suitable alternative to attaching the disc to a calibrated line is to attach it from its centre to a vertical metre stick. Secchi disc visibilities seldom exceed 100 cm in productive fish culture systems, so measurements will seldom be limited because of the length of the metre stick.

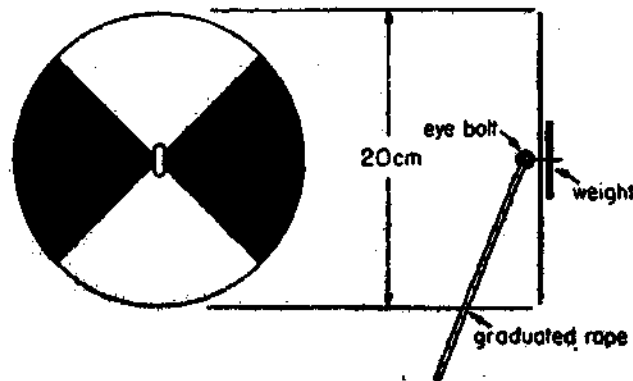


FIG. 7.3. A Secchi disc.

Secchi disc visibility is not a suitable estimate of plankton unless plankton is the primary source of turbidity. An experienced observer can readily distinguish between plankton turbidity and other forms of turbidity. However, the novice must remember that plankton blooms are not always green. Plankton blooms may also impart yellow, red, brown or black colouration to water. Usually plankton organisms are large enough that their particulate nature is obvious if water and its contents are viewed against a white background.

To obtain the secchi disc visibility, lower the disc into the water until it just disappears and record the depth. Lower the disc a little more and then raise it until it just reappears and record the depth. In making these measurements, view the disc from directly above. The average of the two depths is the Secchi disc visibility. Conditions for taking Secchi disc measurements should be standardised. A good practice is to make measurements between mid morning and mid afternoon. The water should be calm and the sun behind you.

TOTAL ALKALINITY

The amount of acid required to titrate the bases in water is a measure of the alkalinity of water. A number of bases occur in water, but total alkalinity results primarily from bicarbonate and carbonate. For the determination of total alkalinity, a water sample is titrated to pH 4.5, the methyl orange end point, with standard acid. The amount of acid required for the titration is equivalent to the alkalinity. Alkalinity is expressed as equivalent calcium carbonate.

Reagents

Methyl orange indicator solution: Dissolve 0.05 g of methyl orange in 100 ml of distilled water.

Standard sodium carbonate, 0.0200N: Dry a few grams of Na_2CO_3 (primary standard) at 140°C and cool in a desiccator. Dissolve 1.0600 g of the Na_2CO_3 and dilute to 1,000 ml in CO_2 -free distilled water. Boil distilled water for 10 to 15 minutes to expel CO_2 and cool before using.

Standard sulphuric acid solution: Prepare a H_2SO_4 solution of approximately 0.1N by diluting 2.8 ml of concentrated H_2SO_4 to 1,000 ml with CO_2 -free distilled water. Dilute 200 ml of 0.1N H_2SO_4 to 1,000 ml with CO_2 -free distilled water. This solution is approximately 0.02N, but it must be carefully standardised to determine its exact normality. To standardise, pipette 10 ml of 0.0200N Na_2CO_3 into a 250 ml beaker. Add 90 ml of CO_2 -free distilled water and 4 to 8 drops of methyl orange indicator solution. Titrate over a white surface to the methyl orange end point with the sulphuric acid solution. At end point, one drop of acid will change the colour of methyl orange from yellow to faint orange. Calculate the normality of the sulphuric acid with the following equation:

$$NV = N'V'$$

Where N = normality of sodium carbonate solution;

V = volume in millilitres of sodium carbonate solution;

N' = normality of sulphuric acid solution;

V' = volume in millilitres of sulphuric acid solution.

Procedure

Add 4 to 8 drops of methyl orange indicator solution to a 100 ml sample and titrate with standard sulphuric acid solution until the colour of the solution changes from yellow to faint orange. Measure the volume of sulphuric acid. Calculate total alkalinity with the following equation :

$$\text{Total alkalinity (mg/litre as CaCO}_3\text{)} = \frac{(T)(N)(50,000)}{S}$$

where T = volume in millilitres of sulphuric acid ;

N = normality of sulphuric acid ;

S = volume in millilitres of sample.

TOTAL HARDNESS

The concentration of calcium plus magnesium expressed as equivalent calcium carbonate is the total alkalinity. Calcium and magnesium ions are titrated with the complexing agent ethylenediamine tetracetic acid disodium salt (EDTA) to form the stable complexes CaEDTA and MgEDTA. The end point of the titration is signalled with an indicator called eriochrome black-T.

Reagent

Buffer solution : Dissolve 67.5 g of NH_4Cl in 570 ml of concentrated NH_4OH . Dilute to 1,000 ml in a volumetric flask with distilled water.

Eriochrome black-T indicator : Dissolve 4.5 g of hydroxylamine hydrochloride and 0.50 g of eriochrome black-T in 100 ml of 70 % ethanol. Prepare fresh every 2 to 3 months.

Standard calcium solution, 0.010 M : Transfer 1.000 g of anhydrous CaCO_3 to a 1,000 ml beaker. Add 1 : 1 HCl slowly to dissolve the CaCO_3 and dilute to about 200 ml with distilled water. Boil for 5 to 10 minutes to expel carbon dioxide, cool and adjust to pH 7, as determined with a pH meter, with 3 N NH_4OH . Transfer to a 1,000 ml volumetric flask and dilute to volume with distilled water.

Standard EDTA solution : Dissolve 4.00 g EDTA disodium salt and 100 mg of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in distilled water and dilute to 1,000 ml. The solution must be standardised against the standard calcium solution. Pipette 10 ml of the standard calcium solution into a 250 ml beaker and add 90 ml of distilled water. Titrate the calcium solution with EDTA solution according to the procedure given below. Compute the molarity of the EDTA solution with the equation : $NV = N'V'$.

Procedure

Measure a 100 ml water sample into a 250 ml Erlenmeyer flask. Add 2.0 ml of the buffer solution and mix. Add 8 drops of eriochrome black-T indicator and titrate with the EDTA solution. At the end point, the solution will change from wine-red to pure blue. Calculate the total hardness with the equation :

$$\text{Total hardness (mg/litre as CaCO}_3\text{)} = \frac{(T) (M) (100, 100)}{S}$$

where T = volume in millilitres of EDTA solution ;

M = molarity of EDTA solution ;

S = volume in millilitres of sample.

Comment

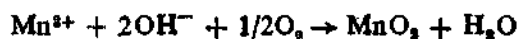
For samples high in hardness, e.g., sea water, dilute a 1.0 to 10.0 ml water sample to 100 ml with distilled water. Use the actual volume of sample in the calculation.

HYDROGEN ION (pH)

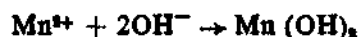
Various types of indicator papers and solutions have been used to measure pH. However, the only reliable technique is the electrometric pH meter. The manufacturer's instructions should be consulted for use of a pH meter. Before making pH measurements, carefully calibrate the meter with a pH 7 buffer. However, this procedure does not verify that the meter will read other pH values correctly. A second buffer, pH 5 if samples are expected to be acidic or pH 9 if samples are expected to be basic, should be used to determine if the pH meter will read a second pH correctly after it has been calibrated at pH 7.

DISSOLVED OXYGEN

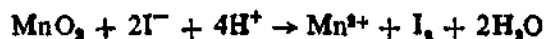
In the basic Winkler procedure, a sample of water is treated with manganous sulphate, potassium iodide and sodium hydroxide. Under highly alkaline conditions, the manganous ion is oxidised by molecular oxygen to manganous dioxide, a brown precipitate.



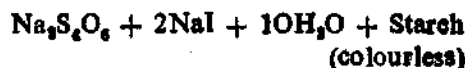
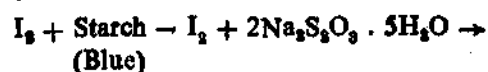
Notice that only one half of the oxygen in manganous dioxide came from molecular oxygen. The formation of a white precipitate will occur even in the absence of oxygen since the manganous ion will form manganous hydroxide, a white precipitate.



Next, sulphuric acid is added to the sample to dissolve the precipitate and produce acid conditions for the oxidation of iodide to iodine by manganous dioxide according to the following reaction :



The quantity of I_2 released is proportional to the amount of O_2 originally present. One half of a molecule of O_2 resulted in the release of one molecule of iodine (I_2). The amount of I_2 is estimated by titration with standard sodium thiosulphate. A starch indicator is used to determine the end point of the titration. As long as iodine is present, the solution is blue. When all the iodine has been titrated the solution becomes colourless.



The amount of iodine is used to calculate the original DO concentration.

Reagents

Manganous sulphate solution : Dissolve 364 g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in distilled water, filter and dilute to 1,000 ml in a volumetric flask.

Alkali-iodine-azide solution : Dissolve 500 g of NaOH and 150 g of KI in distilled water and dilute to 1,000 ml in a volumetric flask. Dissolve 10 g of NaN_3 in 40 ml of distilled water and add to the NaOH-KI solution.

Sodium thiosulphate solution : Dissolve 6.3 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in freshly boiled and cooled distilled water and dilute to 1,000 ml in a volumetric flask. There is no need to weigh the $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ with more precision since the resulting solution must be standardised. Add 5 drops of chloroform as a preservative. This reagent must be restandardised every few days and stored in the dark.

Concentrated sulphuric acid : Analytical reagent grade.

Sulphuric acid solution, 10 percent : Add 5 ml of concentrated H_2SO_4 to 45 ml of distilled water.

Potassium dichromate solution, 0.0250 N : Dry 2 or 3 g of $\text{K}_2\text{Cr}_2\text{O}_7$ at 105°C and cool in a desiccator. Dissolve 0.6129 g of $\text{K}_2\text{Cr}_2\text{O}_7$ and dilute in a volumetric flask to 500 ml with freshly boiled and cooled distilled water.

Starch indicator : Add 2 g of soluble starch to 100 ml of distilled water in a 250 ml beaker. Heat while stirring until transparent and add 0.5 ml of formalin as a preservative.

Procedure

Standardisation of sodium thiosulphate solution : Dissolve 2 g of KI in a H_2SO_4 solution. Use volumetric pipette to measure 10 ml of 0.025 N $\text{K}_2\text{Cr}_2\text{O}_7$ into the flask and place the flask in the dark for 5 minutes. Dilute to 250 or 300 ml with distilled water. Titrate with sodium thiosulphate solution until a pale straw colour is reached. Add 8 drops of starch indicator and titrate until the blue colour of the starch suddenly disappears. Record the volume of sodium thiosulphate used. Calculate the normality with the equation : $NV = N'V'$.

Preparation of sample for analysis : If a bottle train type sampler is used, the BOD bottle must be removed and stoppered carefully to prevent the introduction of air bubbles. If a Van

Dorn or Kemmerer bottle is used, introduce the water through a tube which discharges at the bottom of the BOD bottle, allow the BOD bottle to overflow for two or three exchanges of water and stopper it carefully to prevent air bubbles. Samples must be analysed for DO without delay.

Fixation of dissolved oxygen and liberation of iodine: To a sample in a 300 ml BOD bottle, add 2 ml of manganous sulphate solution and 2 ml of alkali-iodine-azide solution. These reagents may be added with a measuring pipette. Introduce the reagents below the surface of the sample and stopper with care to prevent air bubbles. Mix the solution in the bottle by rapidly inverting it twenty times and then let the sample stand until a precipitate settles to the bottom half of the bottle. Mix again by inverting the bottle several times and let the precipitate settle. Add 2 ml of concentrated H_2SO_4 with a measuring pipette, stopper the bottle and invert several times to dissolve the precipitate.

Titration of iodine: To compensate for overflow of the sample during the addition of the reagents, a 101 ml sample is taken for titration. Calibrate a 100 ml graduated cylinder by measuring 101 ml into it and placing a suitable graduation at the appropriate position above the manufacturer's 100 ml graduation. Shake the BOD bottle and then measure 100 ml into a 250 ml beaker. Titrate with standard sodium thiosulphate solution to a pale straw colour. Add 8 drops of starch indicator solution and titrate until the blue colour disappears. Record the volume of sodium thiosulphate used. Use the following equation to calculate the DO concentrations:

$$\text{Dissolved oxygen (mg/litre)} = \frac{(T)(N)(8,000)}{S}$$

where T = volume in millilitre of sodium thiosulphate;

N = normality of sodium thiosulphate;

S = volume in millilitres of sample.

Comments

Consult a more detailed water analysis manual if there is any question about interference. A sample can be preserved for up

to 8 hours by adding 0.7 ml of concentrated H_2SO_4 and 1 ml of 2% NaN_3 and storing the sample in a sealed BOD bottle at 20°C or less. In completing the procedure, add 3.0 ml of alkali-iodide-azide solution rather than the usual 2.0 ml. Dissolved oxygen may also be fixed at the sampling site by the addition of manganous sulphate and alkali-iodide-azide solution and the sample carried to the laboratory within 2 or 3 hours for prompt completion of the DO determination.

Standard phenylarsine oxide (PAO) may be purchased (Hach Chemical Company, Loveland, Colorado) and used instead of sodium thiosulphate in the titration of DO. PAO does not have to be continually restandardised because it is stable for several months.

CHLOROPHYLL *a*

The phytoplankton in pond water is concentrated by filtration through a membrane filter. The pigments contained in the phytoplankton are extracted in acetone and the concentration of chlorophyll *a* determined spectrophotometrically. A close relationship usually exists between the concentration of chlorophyll *a* in water and the total abundance of phytoplankton,

Special apparatus

The following special items are needed: Millipore filters (Type HA, 47 mm, 0.45 micron pores), millipore filtration apparatus, small electric drill, tissue grinder with 10 ml chamber and Teflon pestle (A. H. Thomas Co., Philadelphia, PA., Cat. No. 3431-E15), centrifuge and spectrophotometer.

Reagents

Acetone 90%: Add 50 ml of distilled water to 450 ml of reagent grade acetone.

Magnesium carbonate suspension 1%: Place 10 g of powdered MgCO_3 in a 100 ml volumetric flask and dilute to volume with distilled water. Only a small amount of the MgCO_3 will dissolve.

Procedure

Place a millipore filter on the filter holder and attach the funnel. Shake the MgCO_3 suspension and pipette 1.0 ml over the filter. Apply vacuum to remove the liquid from the filter. Transfer 50 or 100 ml of the well mixed sample to the funnel. After the sample has filtered through, remove the Millipore filter and trim away the edges which are not coated with residue. Crumple the filter and place it in the tissue grinder. Add 2 ml of 90% acetone and grind for 1 minute, then add 8.00 ml of 90% acetone and grind for 30 seconds. Transfer the contents of the tissue grinder tube to a 50 ml Erlenmeyer flask, stopper and refrigerate in the dark for 1 hour. Pour the acetone extract into a 15 ml test tube and centrifuge at 2,000 to 3,000 revolutions per minute (rpm) for 10 minutes. Decant the acetone extract into a cuvette and centrifuge at low speed (300 to 500 rpm) for five minutes. Measure the absorbance of the acetone extract at 665 nm and again at 750 nm with a spectrophotometer set at 0.0 absorbance with 90% acetone. Calculate the chlorophyll *a* concentration from the equation :

$$\text{Chlorophyll } a \text{ in } \mu\text{g/litre} = 11.9 (A_{665} - A_{750}) \frac{V}{L} \times \frac{1,000}{S}$$

where A_{665} = the absorbance at 665 nm ;

A_{750} = the absorbance at 750 nm ;

V = the acetone extract in millilitres

L = the length of light path in the spectrophotometre in centimetres ;

S = the volume in millilitres of sample filtered.

PARTICULATE ORGANIC MATTER

Glass fibre filters are available which will retain most of the particles in water which are greater than 1 micron in size. When pond water is passed through such a filter, essentially all of the living plankton and much of the particulate matter is retained. The filter and residue are then dried and weighed. Next, the filter and residue are ignited, cooled and weighed again. The weight loss on ignition is taken as the particulate organic matter content of the sample.

Special apparatus

The following special items are required : glass fibre filtration apparatus, 47 mm Gelman Type A-E glass fibre filters or equivalent and a muffle furnace.

Procedure

Prepare glass fibre filters by soaking them in distilled water for 24 hours, drying them and igniting them in a muffle furnace for 20 minutes at 550°C. Place a glass fibre filter on the filter holder, attach the funnel and transfer a well-mixed and accurately measured sample of water to the funnel with a graduated cylinder. The sample volume must be large enough so that the residue retained on the filter will be heavy enough to weigh. A volume of 250 ml is usually adequate for pond waters. Apply vacuum and after the sample has drained through the filter, wash the filter and residue with 20 ml of distilled water. Dry the filter and residue at 103°C, cool in a desiccator and weigh. Ignite the tarred filter and residue at 550°C in a muffle furnace for 20 minutes, cool in a desiccator and weigh again. The weight loss represents particulate organic matter. Use the equation below to calculate the concentration of particulate organic matter.

$$\text{Particulate organic matter (mg/litre)} = (B - A) \frac{1,000}{S}$$

where B = the weight of the filter and residue in milligrams before ignition ;

A = the weight of the filter and residue in milligrams after ignition.

S = volume of sample in millilitres.

CARBON DIOXIDE

Water which has a pH above 8.3 does not contain appreciable carbon dioxide. Therefore, the amount of base required to raise the pH of a water sample to the phenolphthalein end point is approximately equivalent to the carbon dioxide content of the sample.

Reagents

Phenolphthalein indicator solution: Dissolve 0.5 g of phenolphthalein in 50 ml of 95% ethyl alcohol and add 50 mg of CO_2 free water. Add 0.04554 N sodium carbonate dropwise until a faint pink colour appears.

Standard sodium carbonate 0.054 N: Dry a few grams of Na_2CO_3 and dilute to 1,000 ml with CO_2 free distilled water. This solution must be prepared fresh daily.

Procedure

To minimise exposure to air, siphon a portion of the sample into a 100 ml graduated cylinder through a flexible tube which discharges at the bottom of the cylinder. Let 50 to 75 ml of water overflow from the cylinder and remove tube. Remove excess sample from cylinder with a pipette. Add 4 drops of phenolphthalein indicator solution. If the sample turns pink, CO_2 is absent. If sample remains colourless, titrate with Na_2CO_3 while stirring gently with a stirring rod. A faint pink colour that remains for 30 seconds marks the end point. Calculate CO_2 as follows:

$$\text{Carbon dioxide (mg/litre)} = \frac{(T)(N)(22,000)}{S}$$

where T = volume in millilitres of sodium carbonate;

N = normality of sodium carbonate;

S = volume in millilitres of samples.

CHEMICAL OXYGEN DEMAND

In this modification of the COD procedure, no heat other than that produced by the dilution of concentrated sulfuric acid is applied to the sample. In acid solution, potassium dichromate oxidizes organic matter to carbon dioxide and water. The amount of potassium dichromate consumed is equivalent to the quantity of readily oxidizable organic matter in the sample.

Reagents

Potassium dichromate solution 1.000N : Dry primary standard grade $K_2Cr_2O_7$ at $103^\circ C$ for 2 hours and cool in a desiccator. Dissolve 49.036 g of $K_2Cr_2O_7$ in distilled water and dilute to 1,000 ml.

Potassium dichromate solution 0.0250N : Dilute 25.00 ml of 1,000 N $K_2Cr_2O_7$ and 100 mg of sulfamic acid to 1,000 ml with distilled water.

Ferrous ammonium sulphate solution : Dissolve 9.8 g of $Fe(NH_4)(SO_4) \cdot 6H_2O$ in distilled water and add 20 ml of concentrated H_2SO_4 . Cool, dilute to 1,000 ml and store in the dark. Standardise daily as follows. Dilute 10 ml of 0.0250 N $K_2Cr_2O_7$ to about 45 ml with distilled water in an Erlenmeyer flask and add 30 ml of concentrated sulphuric acid. When cool, add 2 or 3 drops of ferroin indicator and titrate with ferrous ammonium sulphate as described in the procedure below. Calculate normality as : $NV = N'V'$.

Ferroin indicator : Dissolve 1.8877 g of 1, 10-phenanthroline monohydrate and 0.7 g of $FeSO_4 \cdot 7H_2O$ in 100 ml distilled water.

Other reagents : Reagent grade silver sulphate, mercuric sulphate and concentrated sulphuric acid.

Procedure

Clean glassware with H_2SO_4 - $Na_2Cr_2O_7$ cleaning solution and rinse thoroughly in distilled water. Pipette a 20 ml sample and 10 ml of the standard dichromate solution (0.025N) into a 125 ml Erlenmeyer flask. A reagent blank is prepared from distilled water and treated exactly as the samples. Add 30 ml concentrated sulphuric acid, 0.4 g Ag_2SO_4 crystals and enough $HgSO_4$ crystals to maintain an $HgSO_4$: chloride ratio of 10. Swirl. Cover flasks with clean cover glasses and let stand for 30 minutes. Dilute with 75 ml of distilled water. Add 2 or 3 drops of ferroin indicator and titrate with standard ferrous ammonium sulphate (0.025N). Initially, samples will vary in

colour (yellowish orange to blue-green), but just before the end point all samples will turn blue-green. At the end point, a single drop of titrant causes the colour to change from blue-green to red-brown. If samples are high in organic matter, use more concentrated solutions of potassium dichromate and ferrous ammonium sulphate. Calculate the COD with the following equation :

$$\text{COD in mg/litre} = \frac{(B - A) (N) (8,000)}{S}$$

where B = millilitres of ferrous ammonium sulphate (FAS) used in the titration of the reagent blank ;

A = millilitres of FAS used in the titration of the sample ;

N = normality of the FAS ;

S = volume in millilitres of sample.

NITRITE

The colorimetric methods generally used for nitrite employ diazotising reagents. Nitrite reacts with these reagents in acidic solution to form diazonium salts. The diazonium salts are coupled with amino or hydroxyl groups of aromatic compounds to form coloured azo compounds. The method given here employs sulphanilamide as the diazotising reagent and N-(1-naphthyl)-ethylenediamine as the coupling reagent. The azo compound is bright pink and a concentration of 0.01 mg/litre $\text{NO}_2\text{-N}$ produces a discernable colour.

Instrument

A spectrophotometer capable of operating at 543 nm is required.

Reagents

Diazotising reagent : Add 5 g of sulphanilamide and 50 ml of concentrated hydrochloric acid to 300 ml of distilled water in a 500 ml volumetric flask. Stir to dissolve and dilute to volume.

Coupling reagent : Dissolve 500 mg of N- (1-naphthyl)-ethylenediamine dihydrochloride in 500 ml of distilled water.

Store in a dark bottle out of the light. This reagent gradually becomes dark brown and must be prepared fresh every 2 to 4 weeks.

Standard nitrite-nitrogen solution 1.00 mg/litre: Dissolve 0.4925 g of NaNO_2 in 1,000 ml of distilled water. This solution contains 100 mg/litre of $\text{NO}_2\text{-N}$. Pipette 10 ml of the 100 mg/litre $\text{NO}_2\text{-N}$ solution into a 1,000 ml volumetric flask and dilute to volume with distilled water to give a 1.00 mg/litre $\text{NO}_2\text{-N}$ solution. These solutions deteriorate rapidly.

Procedure

Development and measurement of pink colour: Filter the water sample through Whatman No. 42 or equivalent, filter paper. Measure 50 ml of water into a 100 ml beaker. Add 1.0 ml of diazotising reagent, stir and allow 2 to 4 minutes (no longer) for reaction. Add 1.0 ml of coupling reagent and stir. Let the solution stand for 10 minutes to form the azo compound, transfer to a 1 cm cuvette and measure the pink colour spectrophotometrically at 543 nm. Use a reagent blank to set the spectrophotometer at 0.0 absorbance (100% transmittance). Obtain the concentration of nitrogen from a calibration graph.

Calibration graph: Use the standard $\text{NO}_2\text{-N}$ solution (1.00 mg/litre) to prepare a series of $\text{NO}_2\text{-N}$ concentrations. The concentrations listed below are suitable for use with a spectrophotometer with a 1 cm light path length.

Nitrite-Nitrogen (mg/litre)	Millilitres of 1.00 mg/litre nitrite- nitrogen standard diluted to 100 ml
0.00	0.00
0.02	2.00
0.04	4.00
0.06	6.00
0.08	8.00
0.10	10.00
0.15	15.00
0.20	20.00

The aliquots of standard nitrite solution must be transferred to volumetric flasks with volumetric pipettes. Add reagents to develop the colour. Use the 0.0 mg/litre solution to set the spectrophotometer to 0.0 absorbance or 100 per cent transmittance and evaluate the pink colour of the other solutions at 543 nm. Plot the data to obtain a calibration graph.

DETERMINATION OF AMMONIA

Reagents

All the reagents are prepared using ammonia free distilled water.

Phenol-alcohol solution : Dissolve 10 g of reagent grade phenol in 100 ml of 95% v/v ethyl alcohol U.S.P.

Sodium nitroprusside 0.5% : Dissolve 1 g of sodium nitroprusside in 200 ml of water.

Alkaline solution : Dissolve 100 g of trisodium citrate and 5 g of sodium hydroxide in 500 ml of water.

Sodium hypochlorite solution : Use a solution of commercial hypochlorite which should be atleast 1.5 N.

Oxidizing solution : Mix 100 ml of sodium citrate solution and 25 ml of hypochlorite solution and use the same day.

Stock standard solution : 0.100 g Ammonium sulphate (A.R. grade) in 1000 ml distilled water. 1 ml = 1.5 μ g at N.

Method

For natural waters, the procedure consists of the successive addition of 2 ml of phenol solution, 2 ml of sodium nitroprusside solution and 5 ml of oxidising reagent to 50 ml of sample, mixing thoroughly after each addition. The color is allowed to develop at room temperature (22-27°C) for 1 hr and the absorbance recorded at 6400 Å in a spectrophotometer with a 10 cm length cuvette. All the glassware used must be cleaned by washing initially with warm dilute hydrochloric acid and rinsing thoroughly with distilled water.

Procedure and calculation

Dilute the standard stock solution to get working standards of 1.5 ; 3.0 ; 4.5 ; 6.0 and 9.0 μg at N concentrations. Measure the absorbance at a wavelength at 6400 A in a spectrophotometer (10 cm cell) and draw a calibration graph. Compare the absorbance of the given sample and calculate the ammonia concentration from the calibration graph.

HYDROGEN SULPHIDE*

Sulphide is found in anoxic waters, where it is formed by microbiological reduction of sulphate ions. The method described here, depending on the formation of methylene blue from dimethyl p-phenylene diamine, is a simple application of a well established colorimetric method for sulphide.

The method is based on the following principle. The acidified sample is allowed to react with dimethyl p-phenylene diamine, with ferric ions as catalyst. A complex oxidation and substitution takes place, resulting in the quantitative incorporation of any sulphide-sulphur present into a heterocyclic dye called methylene blue. The absorption of light by the sample is measured before or after dilution in 1, 5 or 10-cm cells. The method is as nearly sensitive as is theoretically possible and is for direct determination applicable to concentrations upto about 100/ μg at/1 or about 3.2 mg/l. At higher concentrations of hydrogen sulphide the sample has to be diluted with oxygen-free distilled water prior to the analysis.

Reagents

N, N-dimethyl p-phenylene diamine dihydrochloride, p.a. $(\text{CH}_3)_2\text{NC}_6\text{H}_4 \cdot \text{NH}_2 \cdot 2\text{HCl}$ (1, 4) : 1 g is dissolved in about 6 N hydrochloric acid to 500 ml. This acid may be prepared by diluting concentrated HCl (37 per cent, sp. gr. 1.19) with an equal amount of distilled water.

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Ferric chloride, p.a., FeCl_3 : 8 g is dissolved in about 6 N hydrochloric acid (prepared as above) to 500 ml.

Oxygen-free distilled water : A suitable volume of distilled water is boiled for 30 to 60 minutes. Nitrogen gas may be bubbled through the water during the boiling. As the water cools down to room temperature, nitrogen gas must be bubbled through. This water is difficult to store, so it should be prepared just before use.

Sulphide stock solution : A solution of sodium sulphide is prepared with oxygen-free distilled water. Crystals of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ p.a. are quickly washed with distilled water by squirting from a washing bottle. The crystals are dried with filter paper and placed in a pre-weighed, glass stoppered, weighing glass. 0.750 g is weighed on an analytical balance and dissolved in oxygen-free distilled water (added with aid of a siphon) to 1000 ml in a volumetric flask.

Sulphide working solution : Siphon a suitable volume of oxygen-free distilled water into a 500 ml volumetric flask. Into this is pipetted 25 ml of the sulphide stock solution and oxygen-free distilled water is added to the mark. This solution contains approximately $5 \mu\text{g/ml}$ as sulphide, S^{2-} (about $0.156 \mu\text{g at/ml}$). For the greatest accuracy, the concentration is determined by titration. The solution is stable for only 15 – 30 minutes.

Sodium thiosulphate solution, 0.02N : 5g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ p.a. is dissolved in 1000 ml distilled water. Add 5 ml isobutyl alcohol before diluting to the full volume of the volumetric flask.

Potassium hydrogen iodate solution : Weigh out accurately 1.2998 g $\text{KH}(\text{IO}_3)_2$ p.a. dried at 105°C for one hour. Dissolve in distilled water and dilute to 1000 ml. This solution is 0.04 N and very stable.

Sulphuric acid (1 + 1) solution : One volume of acid is carefully mixed with one volume of distilled water under constant cooling and mixing.

Starch solution: 1% or Thyodene indicator as for the dissolved oxygen determination.

Potassium iodide, KI, p.a. crystals.

Equipment

Winkler bottles, Spectrophotometer or filterphotometer with filter at or close to 670 nm. 1 cm and 5 cm or 10 cm cells and automatic syringe pipettes.

Calibration

Standardisation of the thiosulphate, determination of the factor (f): Add 1 g potassium iodide and 2 ml sulphuric acid (1 + 1) to an Erlenmeyer flask with a ground stopper containing approximately 150 ml distilled water. Mix well and add 10 ml of the potassium hydrogen iodate solution by means of a pipette and stopper the flask. Swirl gently and allow the iodine liberation to proceed (away from direct sunlight) for 2-4 minutes. Titrate the iodine with the thiosulphate solution to a pale straw colour. Add two drops of the starch solution as indicator and complete the titration until the disappearance of the blue colour. A blank is run to check the reagents. This is done by repeating the process, but omitting the hydrogen iodate. If v is the millilitres of thiosulphate consumed, then

$$10 - 0.04 = f \cdot v \cdot 0.02 \text{ and } f = \frac{20}{v}$$

The mean value of (f) should be calculated after at least three runs, differing not more than 0.05 ml.

Standardisation of the sulphide working solution: This is carried out within minutes after preparation of the working solution and at the same time as the preparation of the photometric standard samples.

Take six Erlenmeyer flasks with ground stoppers and add to each about 10 ml distilled water and 1-2 g potassium iodide. Pipette into each flask 10 ml hydrogen iodate solution. Add

1.0 ml sulphuric acid (1 + 1) into each flask. Into three of the flasks pipette 50 ml of the sulphide working solution and to the other three add about 50 ml distilled water. Set all flasks aside in a cool place whilst the colorimetric standardisation is commenced and then titrate the contents of the flasks with thio-sulphate using starch indicator.

A = mean of the titrations of three solutions with no added sulphide, in ml.

B = mean of the titrations of the three solutions containing sulphide, in ml.

f = factor of the thiosulphate.

(the individual titrations constituting a triplicate should agree to within 0.05 ml).

$$\text{H}_2\text{S ml/l} = \frac{221.40 \cdot f \cdot (A - B)}{50}$$

To convert this to $\mu\text{gat/ml H}_2\text{S}$ (or rather μ moles, if the result is reported as hydrogen sulphide instead of sulphide, S^{2-}), the number is divided by 22.140:

$$\text{H}_2\text{S } \mu\text{g at/ml} = \frac{10 \cdot f \cdot (A - B)}{50}$$

Photometric standard samples: From the working solution the following standard series is prepared.

To 100 ml measuring flasks or volume calibrated Winkler bottles the following volumes of working solution are added by means of a pipette or burette (Table 7.1):

TABLE 7.1

20 ml	=	100 $\mu\text{g S}^{2-}$	=	31.2 $\mu\text{g at/l S}^{2-}$
16 ml	=	80 " "	=	25.0 " "
12 ml	=	60 " "	=	18.7 " "
8 ml	=	40 " "	=	12.5 " "
4 ml	=	20 " "	=	6.3 " "
0 ml	=	0 " "	=	0.0 " "

These concentrations correspond to the solution with 5 $\mu\text{g/ml}$. Thus they have to be corrected according to the value found by titration.

If Winkler bottles are used the concentration values given above have to be recalculated accordingly for the calibration graph described below.

With the aid of a siphon the bottles are filled up with oxygen-free distilled water to 100 ml mark or in case of calibrated Winkler bottles, to the neck. In the latter case a correction for the volume has to be made for each bottle.

As soon as a bottle is filled up, 1 ml of each reagent is added with an automatic syringe pipette and the contents of the bottle are mixed well. After 60 minutes, the samples are measured against the blank, at 670 nm in 1 cm and/or 5 cm cells, as suitable. From the results a calibration graph for each of the cell lengths is prepared on millimeter paper. The graph should be a straight line and go through origo.

If higher concentrations are analysed, the graph will start deviating from the straight line at 40 - 50 $\mu\text{g at/l}$ (about 1.3 - 1.6 mg/l). The exact point for the start of the deviation depends on the quality of the amine solution. However, if this is taken into account when calculating the analytical results, the graph—and thus the working range of the method—can be extended upto about 100 $\mu\text{g at/l}$ (about 3.2 mg/l).

Procedure

The samples must be taken with plastic water samplers. If these are not available, metallic ones may be used provided that the inner surfaces are plastic-coated.

An ordinary Winkler bottle is filled with the sample in exactly the same manner as described for the dissolved oxygen determination. The reagents diamine and ferric chloride are immediately added with pipettes (preferably automatic syringe pipettes) to the sample. Let the pipette tips extend deep into the sample bottle. The stopper is now inserted avoiding air bubbles.

The blue colour starts developing in a few minutes and the sample is ready for measurement in a photometer after 30 minutes. However, if the sample contains high concentrations of hydrogen sulphide, one hour must be allowed for full colour development. The colour intensity may be regarded as constant for at least 24 hours.

The colour intensity of the sample is measured against distilled water (or compensated for by reagent blanks) at 670 nm using 1 or 5 cm cells as required.

If the sample contains higher concentrations of hydrogen sulphide than 100 $\mu\text{g}/\text{l}$ (3.2 mg/l) it has to be diluted prior to the analysis. This is done by pipetting a suitable volume of the sample into a measuring flask or Winkler bottle containing some oxygen-free distilled water. The pipette tip should extend below the surface of the water. Then more of the siluting water is added by means of a siphon upto the calibrated volume of the flask or bottle. The reagents are added and the sample is then thoroughly mixed. Account has to be taken of the dilution factor when calculating the result of the analysis.

Note: It is difficult to prepare a standard solution of sulphide with a high degree of accuracy. Therefore a systematic error may be included in the analysis. Using the method described, this error will be below 2%.

It seems impossible to obtain a diamine that is not more or less discoloured. However, this does not seem to affect the results. Analysis done at the Fishery Board of Sweden with a one year old brownish diamine solution produced results which differed only slightly from the results obtained with a freshly prepared solution.

According to Strickland and Parsons (1968) it may be necessary to compensate the absorption value of each sample for the absorption value of a reagent blank. This latter value is obtained by adding reagents to filtered surface water and measuring this against the same filtered water containing no reagents. The absorption value should not exceed 0.5 in a 10 cm cell and should preferably be less than 0.25.

LIME REQUIREMENT

Boyd (2, 3) altered a lime requirement procedure for agricultural soils (1) so that it could be used to estimate liming rates for fish ponds. Boyd (2) found that total hardness and total alkalinity of pond waters exceeded 20 mg/litre when the base unsaturation of muds was 0.2 or less. Furthermore, there was a strong correlation between the base unsaturation of pond muds and their pH values and a mud pH of 6.0 corresponded to a base unsaturation of 0.2. Therefore, if the pH of a mud was known, the base unsaturation could be computed from the regression equation relating pH and base unsaturation of muds. The reduction of pH in a buffer solution caused by a known weight of dry mud provided an estimate of total exchange acidity. Neutralization of the total exchange acidity would give a base unsaturation of 0.0. Therefore, the amount of exchange acidity (in milliequivalents) which must be neutralized to lower the base unsaturation to 0.2 — this corresponds to 20 mg/l total hardness and alkalinity in pond water — was calculated as follows :

$$\text{Acidity to be neutralized} = \frac{\text{exchange acidity}}{\text{initial base unsaturation}} \times \frac{\text{desired change in base unsaturation}}{\text{base unsaturation}}$$

Boyd and Cuenco (4) determined that agricultural limestone reacted to a depth of approximately 15 cm in pond muds over a 2 year period and that air-dry weight of the upper 15 cm layer of mud in ponds averaged 1,400,00 kg/ha. The amount of acidity to be neutralised as estimated for the sample may be expanded to give the amount of acidity to be neutralised in the pond mud. The liming rate in kilograms per hectare of CaCO_3 is calculated from the acidity. A liming factor of 1.5 is multiplied by the liming rate, because agricultural limestone is not 100% effective in neutralising soil or mud acidity.

The method developed by Boyd (2) has proven effective and it has been widely used. However, the procedure was developed for ponds in Alabama and relationships between pH and base unsaturation of muds differ geographically. For most accurate results, the relationship between pH and base unsaturation of muds should be determined for a region before the procedure is

used. This is a difficult task that is often impractical. A simple method developed by Pillai and Boyd (5) for determining the lime requirement of pond muds that does not require data on the relationship between pH and base unsaturation is presented. This method involves measuring the total exchange acidity with a buffer and calculating the liming rate necessary to provide a base unsaturation of 0.0. Because this technique will always provide a higher liming rate than necessary, the liming factor of 1.5 is omitted.

Reagents

Buffer solution: Dissolve 20 g p-nitrophenol, 15 g boric acid, 74 g potassium chloride and 10.5 g potassium hydroxide in distilled water and dilute to 2,000 ml with distilled water.

Procedure

Weigh 20 g of air-dry mud that pass a 0.85 mm screen into a 100 ml beaker and add 40 ml of buffer. Stir intermittently for 1 hr and measure the pH to the nearest 0.01 pH unit with a glass electrode. Each 0.1 unit change in pH represents 0.16 meq of acidity. If the equilibrium pH is less than 6.8, the procedure must be repeated using half as much dry mud. Calculate the lime requirement as follows:

$$\text{Liming rate (kg CaCO}_3\text{/ha)} = \text{pH change} \times 5,600$$

NEUTRALISING VALUE OF LIMING MATERIALS

The method provides an estimate of the strength of a liming material in neutralising acidity. Results are in terms of percentage of pure calcium carbonate.

Reagents

Standard hydrochloric acid, 1.000 N.

Standard sodium hydroxide, 1.000 N.

Phenolphthalein indicator solution.

Procedure

Finely pulverize the liming material. Weigh 500 mg into a 500 ml Erlenmeyer flask. Add 25 ml of standard hydrochloric acid — add slowly to prevent splattering. Boil briskly for 5 minutes. Heat on water bath for 30 minutes. Dilute to 100 ml with distilled water and allow to cool. Add a few drops of phenolphthalein indicator and titrate with standard sodium hydroxide to a faint pink colour. Calculate the neutralising value as follows :

$$\text{Neutralising value (\%)} = \frac{(25-T)(N)(5,000)}{S}$$

where T = volume in millilitres of standard NaOH ;

N = normality of standard HCl ;

S = sample weight in milligrams.

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* Out of print.

FERTILIZATION

3.1. Chemical fertilizers

Inorganic fertilizers used in ponds are the same ones used for agricultural crops. Nitrogen, phosphorus and potassium are termed the primary nutrients in fertilizers. The grade of a fertilizer refers to percentages by weight of nitrogen (as N), phosphorus (as P_2O_5) and potassium (as K_2O , also called potash). For example, a 20-20-5 grade fertilizer contains 20% N, 20% P_2O_5 and 5% K_2O . This method of expressing nitrogen, phosphorus and potassium content is traditional rather than descriptive. Fertilizer does not contain elemental nitrogen (N), phosphorus pentoxide (P_2O_5) or potash (K_2O). The use of N, P_2O_5 and K_2O to indicate fertilizer grades originated long ago and has been accepted for practical purpose. Primary nutrients in fertilizers are usually present as relatively simple compounds which dissolve to give nitrate, ammonium, phosphate or potassium ions. The compositions of some common fertilizer materials are given in Table 3.1. Calcium, magnesium and

TABLE 3.1. Composition of some common inorganic fertilizer materials

Material	Content (%)		
	N	P_2O_5	K_2O
Ammonium nitrate	.. 33-35	—	—
Ammonium sulphate	.. 20-21	—	—
Calcium metaphosphate	.. —	62-64	—
Calcium nitrate	.. 15.5	—	—
Ammonium phosphate	.. 11-16	20-48	—
Muriate of potash	.. —	—	50-62
Potassium nitrate	.. 13	—	44
Potassium sulphate	.. —	—	50
Sodium nitrate	.. 16	—	—
Superphosphate (ordinary)	.. —	18-20	—
Superphosphate (double or triple)	.. —	32-54	—

sulfur, which occur incidentally or are intentionally added, are called secondary nutrients in fertilizers. Trace nutrients copper, zinc, boron, manganese, iron and molybdenum may also be present in minute amounts in some fertilizers.

Fertilizers with specific grades are made by mixing appropriate quantities of nitrogen, phosphorus and potassium fertilizers. If all the primary nutrients are included, the mixed fertilizer is said to be a complete fertilizer. Ingredients needed to supply the primary nutrients for 100 Kg of a particular grade seldom weigh 100 Kg. A filler is added to make up the difference in weight. The filler may be an inert material or it may be a neutralizing agent such as limestone, to reduce acidity. Preparation of 100 Kg of 8-8-8 from ammonium nitrate (33.5% of N), triple superphosphate (46% P_2O_5), muriate of potash (60% K_2O) and filler is illustrated below :

- (1) Calculate the amount of ammonium nitrate (35% N) needed to give 8 Kg of N :

$$8 \text{ Kg of N} \div 0.335 = 23.9 \text{ Kg ammonium nitrate.}$$

- (2) Calculate the amount of triple superphosphate (46% P_2O_5) needed to give 8 Kg of P_2O_5 :

$$8 \text{ Kg } P_2O_5 \div 0.46 = 17.4 \text{ Kg triple superphosphate.}$$

- (3) Calculate the amount of muriate of potash (60% K_2O) needed to give 8 Kg of K_2O :

$$8 \text{ Kg } K_2O \div 0.60 = 13.3 \text{ Kg muriate of potash.}$$

- (4) Combined, the three fertilizer materials only weigh 54.6 Kg, so 45.4 Kg of filler must be added to give 100 Kg.

The calculations for preparing mixed fertilizer from basic source materials are slightly more difficult if one of the source materials contains two primary nutrients. The appropriate calculations for preparation of 100 Kg of 20-20-5 fertilizer from diammonium phosphate (21% N and 54% P_2O_5), urea (45% N), and muriate of potash (60% K_2O) are given below :

- (1) Calculate the amount of diammonium phosphate (54% P_2O_5) needed to give 20 Kg of P_2O_5 :

$$20 \text{ Kg} \div 0.54 = 37.0 \text{ Kg diammonium phosphate,}$$

- (2) Calculate the amount of N contained in 37.0 Kg of diammonium phosphate (21% N) :

$$37.0 \text{ Kg} \times 0.21 = 7.8 \text{ Kg N.}$$

- (3) Since the diammonium phosphate supplies 7.8 Kg N, only 12.2 Kg N are needed from urea. Calculate the amount of urea (45% N) :

$$12.2 \text{ Kg} \div 0.45 = 27.1 \text{ Kg urea.}$$

- (4) Calculate the amount of muriate of potash (60% K_2O) required for 5 Kg of K_2O :

$$5 \text{ Kg} \div 0.60 = 8.3 \text{ Kg muriate of potash.}$$

- (5) The three ingredients weigh a total of 72.5 Kg, so 27.5 Kg of filler must be added for 100 Kg of 20-20-5 fertilizer.

In fish culture, it is usually not necessary to mix ingredients and add filler as illustrated above. The appropriate quantities of fertilizer source materials may be calculated, weighed and applied to the pond. For example, suppose that a 1 ha pond must be treated with 20 Kg/ha of 10-20-0 fertilizer and ammonium sulphate (20% N) and triple superphosphate (46% P_2O_5) are available for use. First calculate the amounts of ammonium sulphate and triple superphosphate as follows :

- (1) Since a 10-20-0 fertilizer contains 10 Kg N, 20 Kg P_2O_5 and 0 Kg K_2O , the amounts of N and P_2O_5 in 20 Kg of 10-20-0 are :

$$20 \text{ Kg} \times 0.10 = 2 \text{ Kg N;}$$

$$20 \text{ Kg} \times 0.20 = 4 \text{ Kg } \text{P}_2\text{O}_5.$$

- (2) Calculate the amount of ammonium sulphate (20% N) which contains 2 Kg N :

$$2 \text{ Kg} \div 0.20 = 10 \text{ Kg ammonium sulphate.}$$

- (3) Calculate the quantity of triple superphosphate (46% P_2O_5) needed to give 4 Kg of P_2O_5 :

$$4 \text{ Kg} \div 0.46 = 8.7 \text{ Kg triple superphosphate.}$$

Next, weigh out 10 Kg of ammonium sulphate and 8.7 Kg of triple superphosphate and apply these quantities to the pond.

3.2. Chemical fertilizers and fish production

The use of fertilizers to increase fish yields has an agricultural analogy in the use of fertilizers to favour greater growth of pasture grasses which, in turn, allows increased production to livestock. Therefore, the fish culturist should understand some of the basic principles regulating the beneficial use of fertilizers in agriculture. When a single growth factor is limiting the growth of a plant, the increase in growth with each equal successive addition of the growth factor is progressively smaller. Although slightly more complex, this idea may be extended to more than one growth factor. In crop production, the fertilization rate which results in maximum yield is not necessarily the most

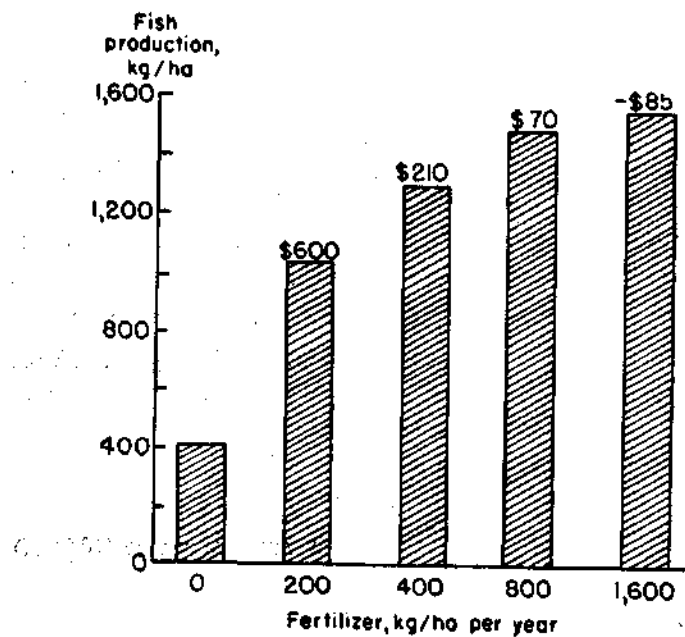


FIG. 3.1. An example of the increase in fish production with increasing fertilizer application rates. The value in dollars per hectare of the increase in fish production above the added cost of the fertilizer is given above the bars representing fish production at progressively increasing fertilizer rates. For calculations, fertilizer was given a value of \$ 0.20 per kilogram and fish a value of \$ 1.00 per kilogram.

economical. After the addition of a few units of fertilizer, the economic value of the increase in crop resulting from another unit of fertilizer may be less than the value of a unit of fertilizer. These same principles apply to fish production (11, 12) and the relationships between fertilizer rate, fish yield and economic value of fish and fertilizer are illustrated in Fig. 3-1.

Since plankton production is most often limited by inadequate phosphorus, phosphate fertilizers are widely used in fish culture (11, 15). In some ponds, it has also been beneficial to include nitrogen fertilizers along with phosphate fertilizers. There has also been limited use of potassium fertilizers in fish production. Increases in fish production resulting from inorganic fertilization differ greatly, but fish production is normally increased by two to five times through proper use of fertilizers (8, 11, 19). Some typical increases in fish production through inorganic fertilization are summarised in Table 3-2.

TABLE 3.2. Typical increases in fish production following fertilization, the factor of increase obtained by dividing production in fertilized ponds by production in unfertilized ponds

Culture species	Factor of increase attributable to fertilizer
<i>Tilapia</i> sp.	3.70
<i>Tilapia</i> sp., <i>Puntius javanicus</i> and <i>Ctenopharyngodon idella</i>	4.38
<i>Lepomis macrochirus</i>	3.37
<i>Cyprinus carpio</i>	1.72 to 8.32

Experience with fertilization of *Tilapia* ponds in Indonesia (11) indicated that the most efficient fertilization programme was the application of 45 Kg/ha of P_2O_5 as annually superphosphate. In Europe, the annual application of 25 to 30 Kg/ha of P_2O_5 , usually as superphosphate has given adequate production of common carp (15). In Israel, common carp and *Tilapia* ponds are fertilized with 60 Kg/ha of ammonium sulphate and 60 Kg/ha of superphosphate at 2 week intervals (9, 10). In Alabama, U.S.A. the most efficient fertilizer schedule for *Tilapia* ponds consisted of biweekly applications of 22.5 Kg/ha of 5-20-5

fertilizer (1). A popular fertilization schedule which is widely used in the southeastern United States is outlined below :

- (1) In mid-February or early March apply 45 Kg/ha of 20-20-5 fertilizer. Follow with two additional applications at 2 week intervals.
- (2) Make three more applications of 45 Kg/ha of 20-20-5 at 3 week intervals.
- (3) Continue applications of 45 Kg/ha of 20-20-5 at monthly intervals or whenever the water clears so that the Secchi disc visibility exceeds 45 to 60 cm.
- (4) Discontinue applications by the last week of October.

The fertilization programme outlined above has been widely used and will produce moderate to dense plankton blooms in most ponds. However, recent research at Auburn University has demonstrated that ponds in well managed pastures often need no fertilization, while woodland ponds almost invariably need to be fertilized for good fish production (2) ; nitrogen and potassium fertilization is not required in many ponds (5, 7; and periodic application of 4.5 Kg/ha of P_2O_5 (10 to 12 applications per year) will give good plankton and fish production in woodland ponds (7, 13).

Research on liquid fertilizers (3, 6, 14) indicates that liquid fertilizers are much more effective than traditional granular fertilizers for increasing fish production in ponds. A summary of this research is provided in Table 3.3. Data show that 2.2 kg/ha

TABLE 3.3. *Production of Sunfish in experimental ponds at Auburn University, Auburn, Alabama*

Fertilizer treatment	Type	P_2O_5 (kg/ha)	Sunfish (kg/ha)
None	..	0	112
20-20-5	.. Granular	9	359
0-20-5	.. Granular	9	321
13-38-0	.. Liquid	2.2	309
13-38-0	.. Liquid	4.4	315
13-38-0	.. Liquid	9	418

of P_2O_5 in liquid fertilizer is just as effective as 9 kg/ha of P_2O_5 in a granular fertilizer.

Plankton can quickly absorb phosphorus from water. In fact, plankton can absorb 50% or more of the phosphate added in a normal fertilizer application within 24 hours (6). When fertilizer granules are broadcast over pond surfaces (the usual method of application), the granules settle immediately to the bottom and the phosphorus is quickly absorbed by mud as it dissolves. Therefore, much of the phosphorus from granular fertilizers never reaches the water for absorption by the plankton.

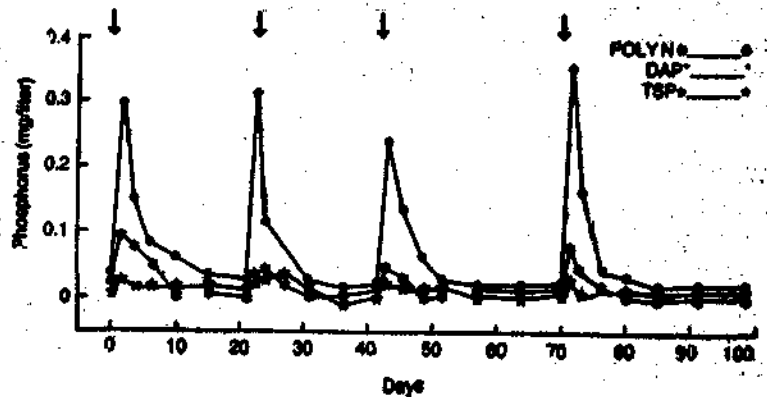


FIG. 3.2. Concentrations of soluble inorganic phosphorus in water of three ponds treated with either fluid fertilizer (Poly N), diammonium phosphate (DAP) or triple superphosphate (TSP) at rates of 9 lbs P_2O_5 /ha/application. Arrows indicate application dates.

This problem is overcome by use of liquid fertilizers. Phosphorus was applied to ponds of identical depth at 9 kg/ha of P_2O_5 per application (6). Concentrations of phosphorus were much higher when liquid fertilizer was the source of phosphorus rate than triple superphosphate or diammonium phosphate (Fig. 3.2). Although phosphorus concentrations declined to similar low values in all ponds within 2 or 3 weeks after application, the high initial concentration of phosphorus in the pond treated with liquid fertilizer would favour rapid uptake of phosphorus by plankton. Another study (14) showed that phosphorus concentrations fertilized at 2.2 kg/ha of P_2O_5 with liquid fertilizer had phosphorus concentrations as high as ponds fertilized at 9 kg/ha of P_2O_5 with granular triple superphosphate.

It is unreasonable to assume that a single fertilizer application rate would be the most effective one under all conditions. Ponds vary greatly in morphometry, hydrology, bottom muds, water quality and type of fish culture, so their response to a given fertilization programme vary greatly. To use an agricultural analogy, it is common knowledge that fertilizer requirements of different fields and crops differ greatly. Fertilization recommendations based on soil analyses have been calibrated against crop responses and the results of soil analyses are used to establish fertilizer rates. Calibration must be conducted for individual crops and for specific soil associations. The nature of different pond muds and waters no doubt varies as greatly as do the characteristics of soils, so a fertilizer rate which works perfectly well in ponds at Auburn, Alabama, may be entirely unsuitable for ponds in another locality. Unfortunately methods for determining the fertilizer requirements of individual ponds are not available. The reader may use the results reported above as guidelines to establish a suitable fertilization programme for a given pond. The abundance of plankton measured by Secchi disc visibility may be used to determine if a particular fertilizer application rate is suitable. This allows for adjustments in the rate without having to wait until fish are harvested to determine if the initial application rate was successful.

3.3. *Methods of application*

Large applications of fertilizers at long intervals are wasteful because much of the phosphorus is absorbed by the mud and nitrogen is lost through denitrification (4). In the United States, fertilizers have traditionally been applied at 2 to 4 week intervals. Fertilizers may be broadcast over shallow water areas of the pond. Fertilizers can be applied more efficiently by placing them on underwater platforms such as the one shown in Fig. 3-8. This method of application prevents phosphorus fertilizer from settling to the pond bottom where the phosphorus is rapidly absorbed by mud. Platforms should be about 30 cm underwater and one platform is adequate for 2 to 4 hectares of pond area. Fertilizer is simply poured on the platform and water currents distribute nutrients as they dissolve.

Liquid fertilizers are heavier than water, so they will flow to the bottom if poured directly into the water. They can be mixed 1:3 with water and splashed around the edges of ponds, or they can be discharged through a tube into the propeller wake of an outboard motor as the boat is navigated over the pond.

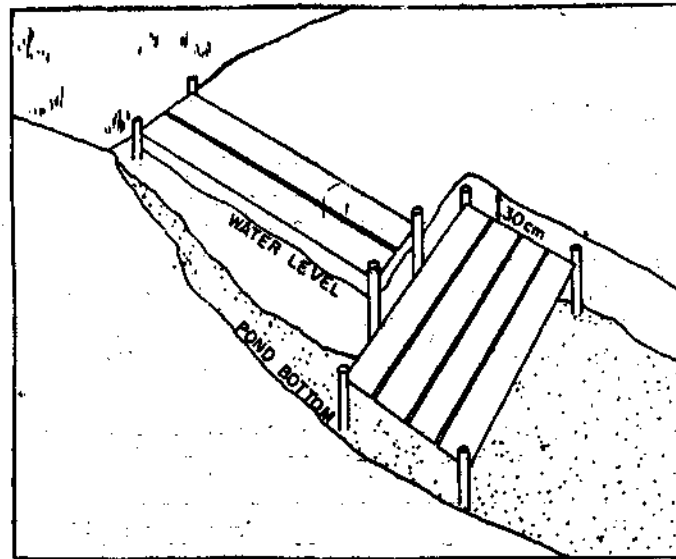


FIG. 3.3. A fertilizer platform.

Ponds with muddy water or water stained with humic substances in which the Secchi disc visibility is less than 30 cm will not respond to fertilizer nutrients because of inadequate light for plankton growth. Weed control must be effected in ponds that are choked with macrophytes or fertilizers will stimulate macrophytes instead of plankton. If the retention time of water in a pond does not exceed 3 or 4 weeks, fertilizer nutrients will be flushed out of the ponds before they produce plankton. Finally, ponds with acid muds and total alkalinity below 15 or 20 mg/litre may not respond to inorganic fertilization unless lime is first applied.

Some other factors must also be considered when using fertilizers. New ponds which have never been fertilized may

require more fertilizer than older ponds that have a history of fertilization. Obviously, fertilization is not effective in flowing waters. In ponds where fish obtain their food almost entirely from feeds, little or no fertilizer should be applied. Some fertilizers are acid forming (urea, ammonium sulphate and ammonium nitrate) and their continued use may result in decreased alkalinity and pH. The acidity of nitrogen fertilizers can be counteracted by liming.

3.4. Organic fertilizers

Organic fertilizers consist of various animal manures or plant wastes and are usually called manures. Organic materials may serve as direct sources of food for fish food organisms and fish, or they may decompose and the inorganic nutrients released may cause plankton blooms. Organic fertilizers have very low N, P_2O_5 , and K_2O contents (Table 3.4) and tremendous quantities are required to supply the same amounts of fertilizer nutrients

TABLE 3.4. Fertilizer constituents in fresh manure of selected farm animals — after Morrison (46)

Type of manure	Average Composition (%)			
	Moisture	N	P_2O_5	K_2O
Dairy cattle	.. 85	.5	.2	.5
Beef cattle	.. 85	.7	.5	.5
Poultry	.. 72	1.2	1.3	.6
Swine	.. 82	.5	.3	.4
Sheep	.. 77	1.4	.5	1.2

found in small quantities of chemical fertilizers. When added to ponds, manures decay and exert an oxygen demand and excessive applications may result in depletion of dissolved oxygen. The rate of oxygen consumption by manure varies with the type of manure and water quality, so the fish culturist must work out safe application rates for a particular manure through trial and error or experimentation.

Organic fertilizers are not widely used in the United States, but they receive extensive use in many other countries. Manures

frequently represent waste products and may be beneficially used in fish culture. However, because of labour and transport costs they may be as expensive per unit of N, P_2O_5 and K_2O as

TABLE 3.5. *Production of Bluegill (Lepomis macrochirus) in ponds fertilized with organic fertilizers and inorganic fertilizer — After Smith and Swingle (60, 62)*

Type of fertilization	Bluegill (Kg/ha)
Cottonseed meal 1,160 kg/ha	423
Cow manure 9,000 kg/ha	272
Kudzu hay 9,000 kg/ha	176
Inorganic fertilization 8-8-8, 1,100 kg/ha	341

chemical fertilizers. Fish production may be similar or even greater in ponds treated with manures than in ponds treated with chemical fertilizers (Table 3.5). This is especially true with the species such as Tilapia that will feed directly on the manure.

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PREFACE

Water quality management forms an integral aspect of aquaculture operations. An understanding of the complex interactions continuously taking place between the ecosystem and the stocked organism is essential to enhance the survival and production by appropriate manipulation of the aquatic environment. Water quality is also of critical importance in enhancing seed production rates in hatcheries and nursery systems. The same also assumes considerable significance in controlling water pollution problems as well as environmental contamination from metabolites and oxygen depletion in culture systems. In India not much work has been carried out on such aspects as aeration, fertilization and liming in aquaculture systems.

We were happy that Dr. Claude E. Boyd, Professor, Department of Fisheries and Allied Aquacultures, Auburn University, Alabama, U.S.A., an authority on Water Quality Management, visited the Centre of Advanced Studies in Mariculture for a brief period in December 1984 as an expert consultant to afford advice and suggestions on the subject to upgrade research, education and Water Quality Management. During this period a four day Workshop was organised and conducted by Prof. Boyd, the course programme which covered in depth the problems on Water Quality Management. Selected aspects pertaining to the environmental conditions were examined and critically evaluated in the course of the Workshop, especially vital aspects such as feeding and water quality, fertilization and liming, dissolved oxygen demand and aeration in culture ponds.

This manual was prepared in connection with the Workshop conducted by Prof. Boyd. It is practically difficult to give coverage to all the water quality problems in aquaculture in a manual like this. However, all essential aspects including methods for water analysis and dose calculations are included in

this publication. It is hoped that the students, scientists and aquaculture entrepreneurs will be immensely benefited by this manual in handling Water Quality Management problems in aquaculture activities.

I express my sincere thanks to Prof. Claude E. Boyd for preparing this manual and the various suggestions regarding Water Quality Management. I thank Shri V. Kunjukrishna Pillai, Scientist and counterpart to Dr. Boyd for the assistance given in the preparation of the manual as well as for the keen interest shown in the conduct of the Workshop.

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22 March 1985.

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